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# Synthetic methods

## Part (ii): Oxidation and reduction methods

Simon E. Lewis

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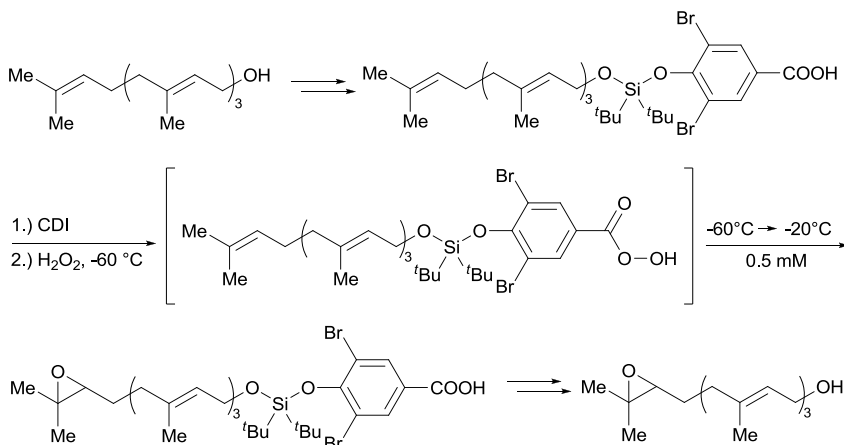
This Report highlights advances in some of the most commonly used oxidation and reduction reactions, focusing on the literature from 2008. Significant advances in oxidation chemistry include site-selective epoxidation of polyprenols,<sup>6</sup> bis(hydroxamic acid) ligands for vanadium(V)-catalysed highly enantioselective epoxidation of *cis*-disubstituted olefins,<sup>40</sup> a direct catalytic aziridination of styrenes with ammonia<sup>112</sup> and an aerobic ruthenium-catalysed alkene to aldehyde oxidation displaying non-Wacker regiochemistry.<sup>133</sup> Significant advances in reduction chemistry include adaptive supramolecular “METAMORPhos” ligands for asymmetric alkene hydrogenation,<sup>160</sup> early main-group metal catalysts for alkene hydrogenation<sup>181</sup> and the use of “frustrated Lewis pairs” to effect H<sub>2</sub> bond scission for imine and nitrile reduction.<sup>191</sup>

### 1 Oxidation reactions

#### 1.1 Alkene epoxidation

2008 has seen the publication of reviews on aspects of epoxidation chemistry from Shi<sup>1</sup> (ketone and iminium organocatalysts), Lincic<sup>2</sup> (heterogeneous catalysis), Katsuki<sup>3</sup> (Ti(salan) complexes) and Walsh<sup>4</sup> (tandem one-pot synthesis of epoxy alcohols). Oyama has also edited a book on epoxidation mechanisms.<sup>5</sup>

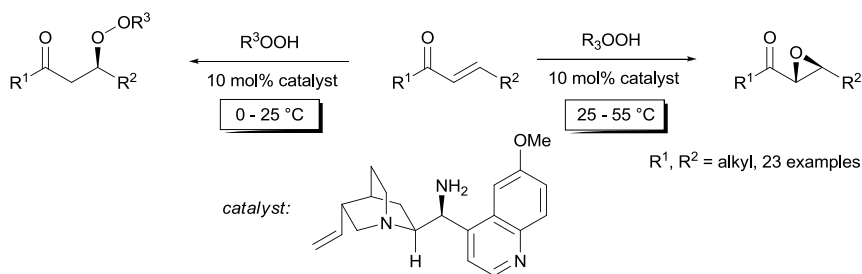
Corey and Gnanadesikan have reported a strategy for the site-selective epoxidation of polyprenols that utilises silyl ether-linked aryl peracids to effect intramolecular epoxidation.<sup>6</sup> The method uses specific aryl motifs that may be varied to effect epoxidation of differing polyprenol double bonds (Scheme 1).



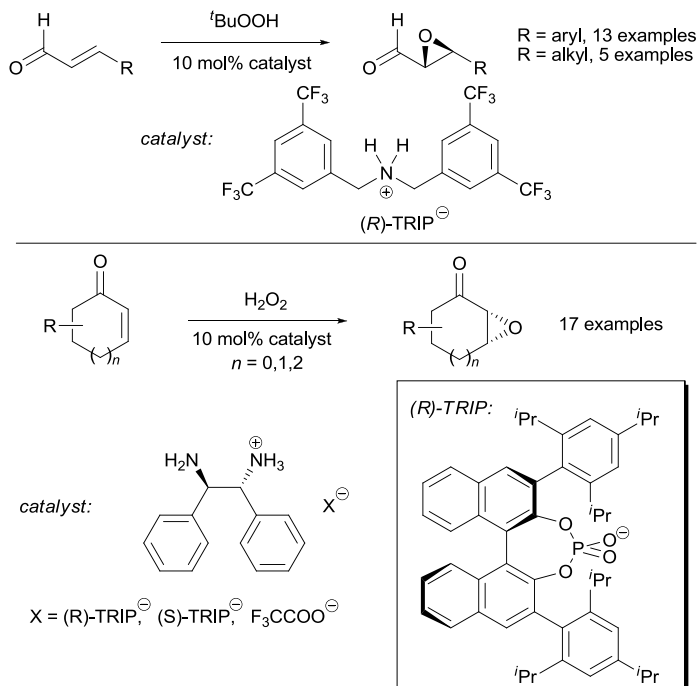
Scheme 1

The reactions are run at high dilution (0.5 mM) to minimise intermolecular oxygen transfer with respect to the desired intramolecular process. Corey and Gnanadesikan<sup>30</sup> report achieving 92% selectivity for the  $\Delta^{14}$  olefin in a pentaprenol, or 89% selectivity for the  $\Delta^{18}$  olefin in a hexaprenol when employing a biaryl peracid.

2008 has seen several advances in organocatalytic asymmetric alkene epoxidation. Deng and co-workers have reported a catalytic asymmetric epoxidation of  $\alpha,\beta$ -unsaturated ketones, employing a cinchona alkaloid-derived catalyst for *in situ* iminium formation.<sup>7</sup> Significantly, reaction conditions have been optimised such that a simple change in reaction temperature is sufficient to alter the course of the reaction from epoxidation to peroxidation; in both instances up to 97% e.e. was achievable. (Scheme 2). The List group independently and simultaneously developed an extremely similar catalytic system.<sup>8</sup>



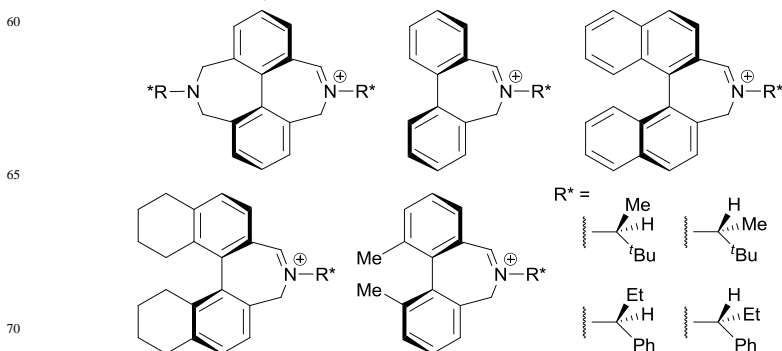
Scheme 2



Scheme 3

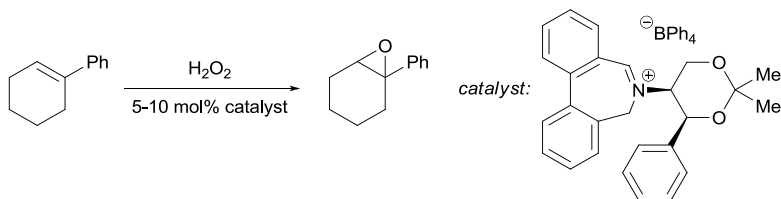
The List research group has disclosed two significant developments in the area. The first employs “asymmetric counterion-directed catalysis” (ACDC) to effect highly enantioselective epoxidations of  $\alpha,\beta$ -unsaturated aldehydes.<sup>9</sup> A transient  $\alpha,\beta$ -unsaturated iminium species is formed, with an axially chiral biaryl counteranion, which then undergoes nucleophilic epoxidation. Both aryl- and alkyl-substituted  $\alpha,\beta$ -unsaturated aldehydes are *viable* substrates, with the former giving superior stereinduction – up to 96% e.e. (Scheme 3). The second report discloses related methodology for the catalytic asymmetric epoxidation of cyclic enones,<sup>10</sup> although in this case the catalyst that is employed contains a homochiral cation in addition to the same biaryl anion. Once again, good enantioselectivity is observed, up to 99% e.e.

The Lacour group have also investigated axially chiral biaryl asymmetric epoxidation catalysts and have undertaken a detailed study to identify biaryl azepinium salts that are effective catalysts, the active species being an oxaziridinium ion generated *in situ* with oxone.<sup>11</sup> They have demonstrated a relationship between the biaryl dihedral angles and the extent of asymmetric transfer. The classes of structures investigated are shown in Scheme 4; up to 92% e.e. has been achieved for certain trisubstituted aryl alkenes.



Scheme 4

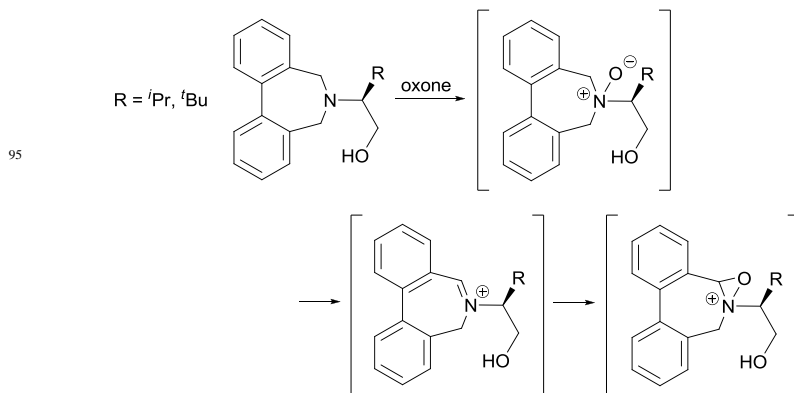
Page and co-workers have also studied biaryl azepinium salts and have reported a new application of a catalyst with an *N*-substituent possessing both an  $\alpha$ - and a  $\beta$ -stereocentre<sup>12</sup> (Scheme 5). Specifically, this system is able to utilise dry hydrogen peroxide (which is superior to oxone in terms of stability and solubility) for generation of the active oxaziridinium species. Optimised reaction conditions are reported for the epoxidation of phenylcyclohexene, with e.e. values up to 56% being obtained. Interestingly, the reaction is believed to involve an unusual double catalytic cycle.



Scheme 5

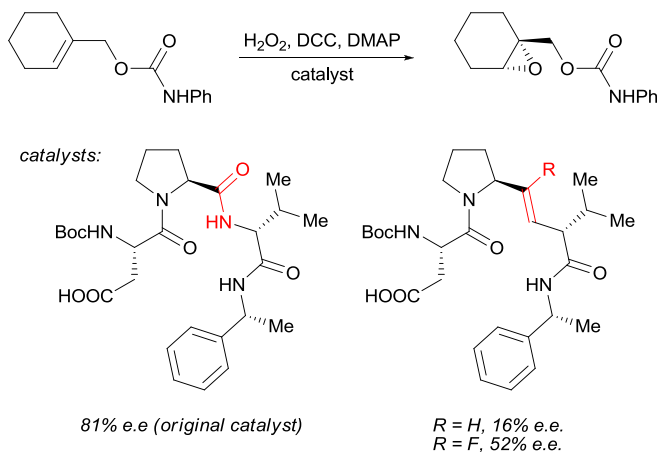
A joint publication from Page and Lacour examines biaryl azepines (as opposed

to azepinium salts) with an *N*-substituent containing a hydroxyl group.<sup>13</sup> In conjunction with oxone, these act as catalysts for epoxidation of di- and tri-  
 85 substituted olefins. Stereoselectivities of up to 81% e.e. are reported. Spectroscopic evidence is reported that is suggestive of the presence of iminium ions in the reaction mixture. The authors thus postulate that oxone effects oxidation of the amine catalyst to the corresponding iminium ion (*via* the *N*-oxide) and that the catalytically active species is therefore actually an oxaziridinium ion, as per the two  
 90 preceding examples (Scheme 6).



**Scheme 6**

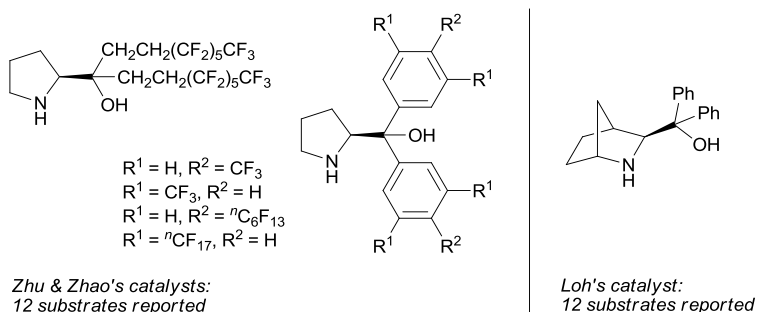
Miller and co-workers have shown previously<sup>14</sup> that aspartate-containing oligopeptides can act as highly enantioselective catalysts for electrophilic alkene  
 100 epoxidation (by intermediacy of the corresponding peracid). In 2008 they reported a comprehensive functional analysis of such systems, in which each amide motif was substituted in turn with an isosteric alkene in order to delineate the relative importance of H-bonding for each peptidic linkage (both intra- and intermolecular). In so doing they were able to identify the region most crucial for catalyst-substrate interaction (Scheme 7).



**Scheme 7**

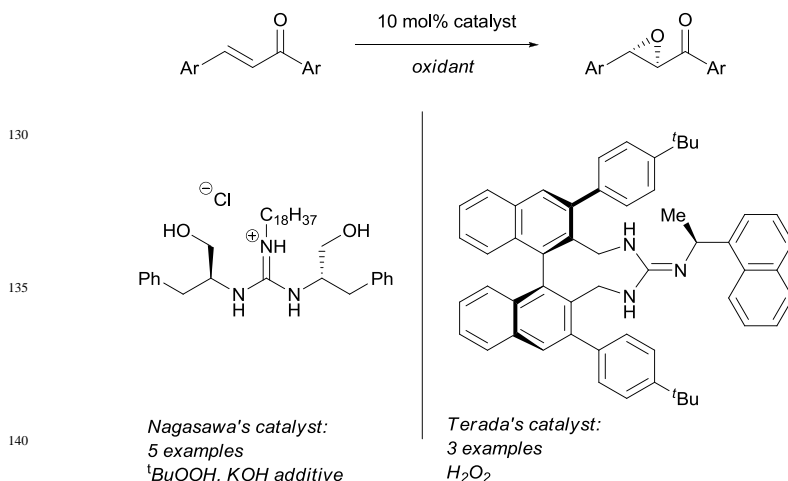
Three reports have appeared in 2008 on the use of amino alcohols as

organocatalysts to effect asymmetric epoxidation of  $\alpha,\beta$ -unsaturated ketones by means of iminium formation. Zhu, Zhao and co-workers have reported the use of fluorine-containing prolinol derivatives to effect epoxidation of chalcones in up to 92% e.e. (Scheme 8).<sup>15</sup> In a similar vein, Loh and co-workers reported the use of a 2-azanorbornyl-3-methanol derivative for epoxidation of chalcones, achieving up to 88% e.e. (Scheme 8).<sup>16</sup> Finally, Lattanzi has disclosed a comparative study of numerous amino alcohols, both cyclic and acyclic, as potential catalysts for asymmetric epoxidation of chalcones; e.e. values up to 52% were obtained.<sup>17</sup>



**Scheme 8**

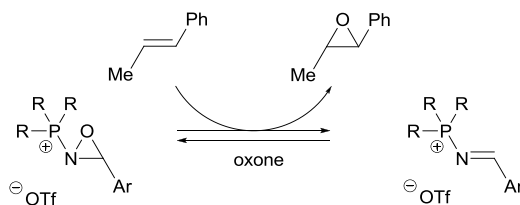
Two Japanese groups have reported uses of guanidines as asymmetric epoxidation catalysts. The Nagasawa group have reported a bifunctional hydroxylguanidine which is an effective organocatalyst for epoxidation of chalcones (Scheme 9).<sup>18</sup> Stereoselectivity up to 73% e.e. is reported. Similarly, the Terada group have reported an axially chiral biaryl guanidine for epoxidation of chalcones (Scheme 9 also).<sup>19</sup> In this instance e.e. values up to 65% have been reported, with hydrogen peroxide being employed as oxidant, as opposed to *tert*-butyl hydroperoxide in the previous case.



**Scheme 9**

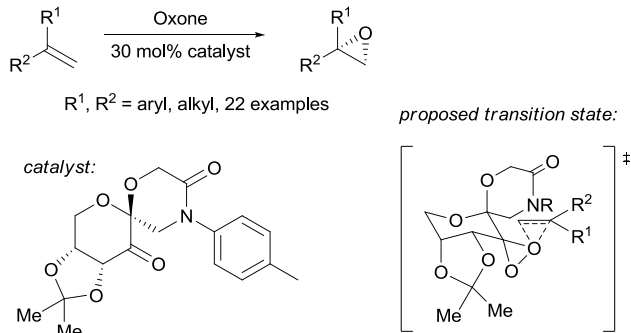
Baceiredo and Kato have reported the use of *N*-phosphonio imines as novel

organocatalysts for alkene epoxidation (Scheme 10).<sup>20</sup> The catalytic activity of the *N*-phosphonio imine can be tuned easily by variation of the *P*-substituents or the imine component and they can be formed *via* a facile two-step process from *N*-silyl imines. 99% conversion was observed for the epoxidation of phenylcyclohexene and the authors state that development of an asymmetric variant of the reaction is underway. The approach is related to that reported by Jennings and Sepulveda-Arques, which employs *N*-phosphinoyloxaziridines.<sup>21</sup>



Scheme 10

Several advances have been reported in the field of dioxirane-mediated asymmetric alkene epoxidation. Shi has disclosed<sup>22</sup> a catalyst comprising a glucose-derived lactam-containing ketone, which undergoes dioxirane formation *in situ*. In contrast to earlier carbohydrate-derived ketone catalysts, this lactam system is able to effect the epoxidation of 1,1-disubstituted olefins with good enantioselectivity. The authors propose that for such substrates the reaction proceeds *via* a planar transition state (Scheme 11).

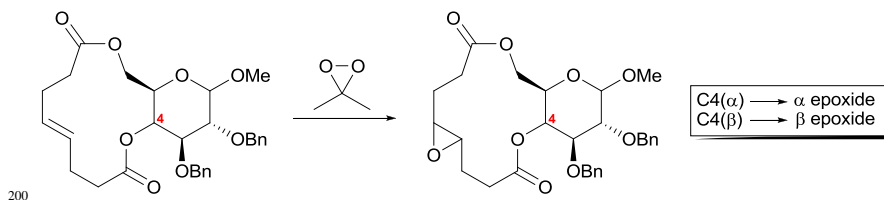


Scheme 11

The Vidal-Ferran group have reported another carbohydrate-derived catalyst as a dioxirane precursor, in this instance a ketone *hydrate*; its selectivity in the epoxidation of aryl alkenes has been studied.<sup>23</sup> The group has also reported a mechanistic study of epoxidation with Shi-type catalysts.<sup>24</sup> Isotopic labelling with <sup>18</sup>O was employed to probe the origins of the stereoselectivity and it was determined that catalyst mediates the transfer of the pro-*S* oxygen of the transient dioxirane species to the alkene in a doubly stereoselective manner. Also published in 2008 were two theoretical studies of dioxirane-mediated alkene epoxidation. Curci, Gandolfi and co-workers undertook a study contrasting dimethyldioxirane (DMDO) with methyl(trifluoromethyl)dioxirane (TFDO).<sup>25</sup> Epoxidations mediated by these two species were modelled by DFT. Rate data, from which Hammett *p*-values were

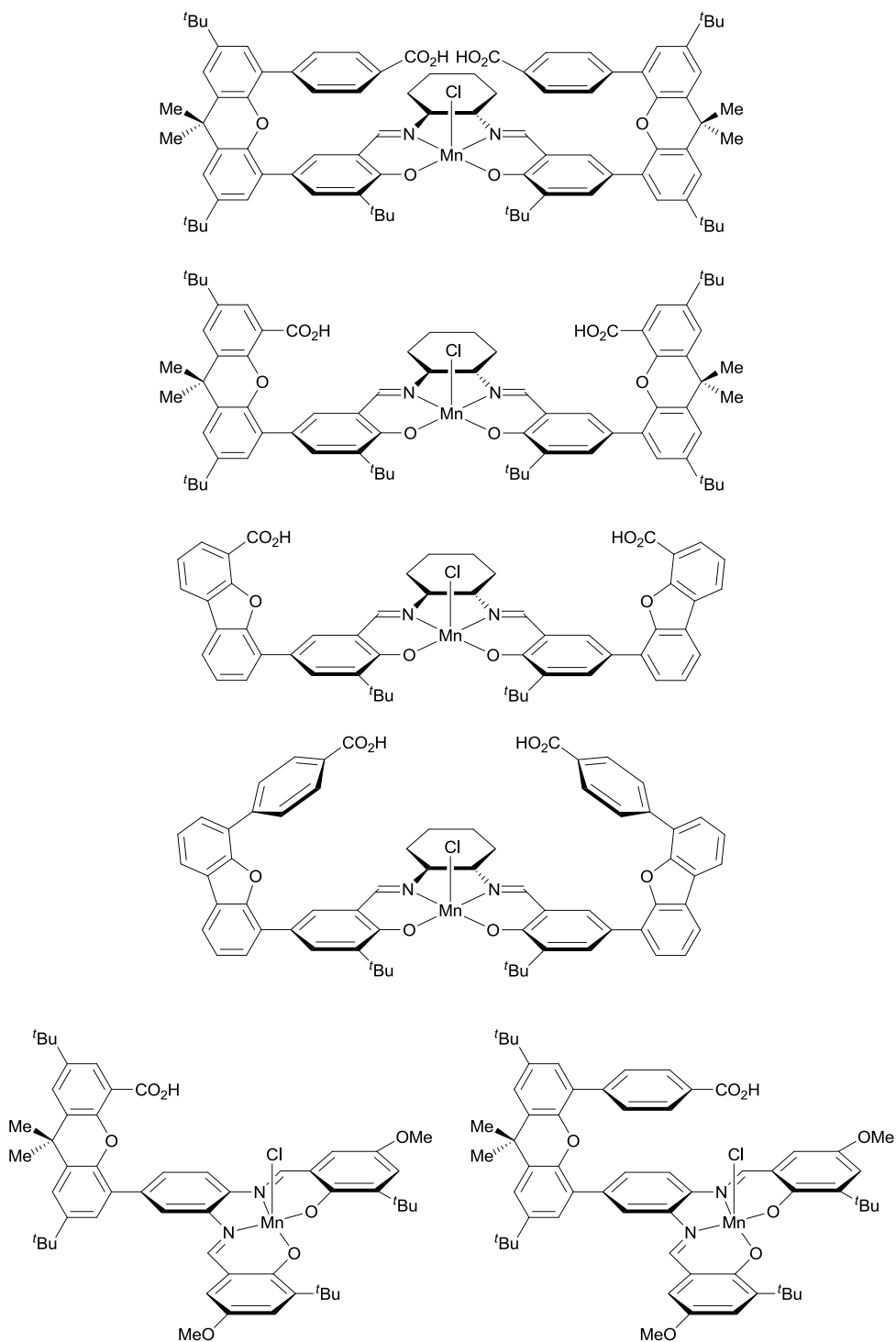
estimated, confirm the electrophilic nature of the oxidant; the enhanced electrophilicity of TFDO with respect to DMDO paralleled the cathode reduction potentials for the two dioxiranes, as measured by cyclic voltammetry. A complementary report, from Werz, examines not the effect of dioxirane substituents but that of alkene substituents<sup>26</sup> – numerous alkenes, ranging from electron-rich to electron poor, were modelled by DFT and in all cases a net charge transfer from the alkene to the dioxirane was observed, again confirming the electrophilic character of DMDO.

Substrate-induced stereoselectivity in alkene epoxidation with an achiral dioxirane (DMDO) has been examined by Peczu for two specific substrate classes. It was found that epoxidation of carbohydrate fused [13]-macrolactones was highly diastereoselective, with good stereoinduction from a remote stereocentre, the carbohydrate C4 position<sup>27</sup> (Scheme 12). Also, in collaboration with Hadad, carbohydrate-based oxepine glycals have been examined.<sup>28</sup> A combination of DFT modelling and experimental results have enabled the formulation of empirical rules for predicting the favoured face of epoxidation for highly substituted cyclic enol ethers. Glycals have also been examined as substrates for stereoselective epoxidation by Gammon and Sels, who have disclosed the tandem epoxidation-hydrolysis or epoxidation-alcoholysis of numerous glycals of varying configuration.<sup>29</sup>



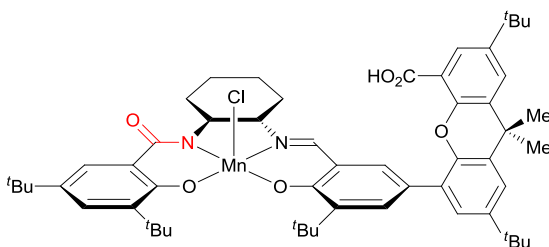
The field of metal-catalysed alkene epoxidation has been equally active in 2008. There have been numerous reports of the use of salen ligands in conjunction with various metals. Li and co-workers have reported nonsymmetric salen ligands wherein an azacrown ether is appended to one of the Schiff base motifs, and have shown that these effect epoxidation when chelated to Mn or Co; dioxygen affinities of the complexes have also been studied.<sup>30</sup> The Liese group has reported salen ligands conjugated to poly(ethyleneglycol) fragments, which they have employed (chelated to Mn or Co) for both alkene epoxidation (achieving up to 95% e.e. for a chromene substrate) and hydrolytic kinetic resolution.<sup>31</sup> Tomaselli and co-workers have employed Jacobsen's Mn(III)salen catalyst with NaOCl as oxidant in aqueous media, employing a surfactant (diethyltetradecylamine *N*-oxide) to enable epoxidation of  $\beta$ -alkyl styrenes in up to 91% e.e.; the surfactant loading is low with respect to substrate.<sup>32</sup> Sun and co-workers have adopted the approach of immobilising a bis(sulfonato)(salen)Mn(III) catalyst on silica, which they then employed in ionic liquids, with NaOCl as oxidant for the epoxidation of styrene and  $\alpha$ -methyl styrene, claiming e.e. values up to 100%.<sup>33</sup> Immobilisation of a (salen)Mn(III) catalyst in silica was also reported by Amarasekara and co-workers, who employed a sol-gel process.<sup>34</sup> Stereoselectivity up to 86% e.e. was observed for epoxidation of aryl alkenes, and the authors note that such enantioselectivity was superior to that observed with the non-immobilised analogue.





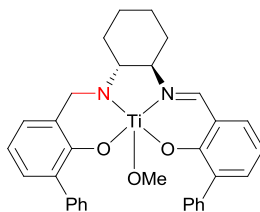
Scheme 13

Also in the salen area, Nocera *et. al.* have reported further examples of  
 225 “Hangman” salen complexes, in which an acid-base group is “hung” over the redox  
 platform of the salen complex. The Nocera group have synthesised salen complexes  
 with various dibenzofuran and dibenzopyran appendages to probe the effects of  
 altering the spatial arrangement of the hanging group and the metal. Both groups  
 “hung” from the salicylyl ring and from the diamine ring have been examined<sup>35</sup>  
 230 (Scheme 13). The authors examined the hangman complexes’ ability to effect alkene  
 epoxidation and H<sub>2</sub>O<sub>2</sub> disproportionation. In a separate publication, Nocera and  
 Yang report appending a single “hanging” group to modified salen-type ligands,  
 comprising an amide and an imine linkage<sup>36</sup> (Scheme 14). Although these complexes  
 are derived from a homochiral diamine, when employed in the epoxidation of 1,2-  
 235 dihydronaphthalene, only racemic product was isolated.



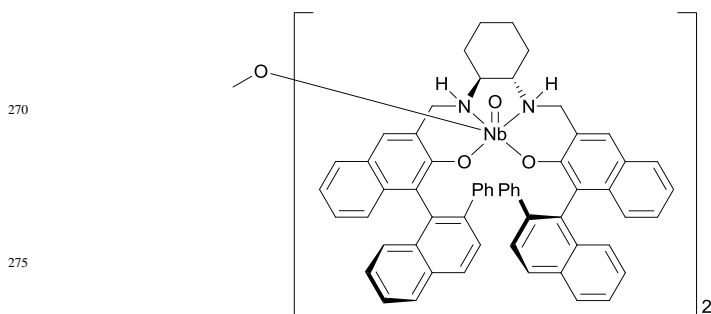
**Scheme 14**

Progress has also been reported in the area of reduced salen ligands. The  
 245 Berkessel group have published a detailed study of a (salalen)Ti complex<sup>37</sup> (Scheme  
 15). Partly reduced “salalen” ligands comprise an imine and an amine linkage. The  
 complex is able to effect epoxidation of electron-rich olefins and the authors  
 describe their investigations into the oxidative degradation of the complex, by mass  
 spectrometric and isotopic labelling experiments; the authors note that the analogous  
 250 more highly oxidised (salen)Ti complex is catalytically inactive.



**Scheme 15**

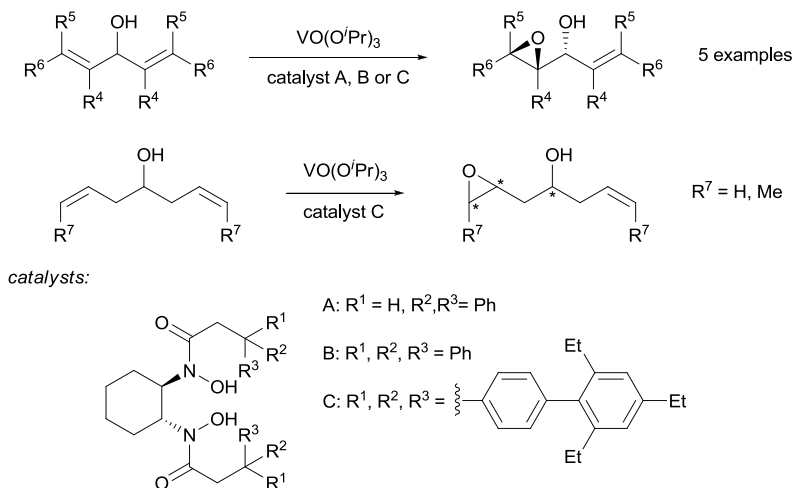
Two significant reports from Katsuki concern fully-reduced “salan” ligands  
 260 (comprising two amine linkages). Katsuki’s group has reported the first asymmetric  
 epoxidation of allylic alcohols employing H<sub>2</sub>O<sub>2</sub> as oxidant.<sup>38</sup> The oxidations are  
 effected by a dimeric Nb(salan) complex, where the ligand contains stereochemical  
 information not only in the 1,2-diamine salan backbone but also in two axially-chiral  
 265 biaryl moieties (Scheme 16). Stereoselectivity of up to 83% e.e. has been achieved  
 for both tri- and *cis*, *trans* and 1,1-disubstituted allylic alcohols.



**Scheme 16**

A second report from Katsuki concerns the mechanism of a previously reported  
 280 asymmetric epoxidation effected with a (salan)Ti complex.<sup>39</sup> They have isolated an  
 unusual  $\mu$ -oxo- $\mu$ - $\eta^2$ : $\eta^2$ -peroxo titanium complex, which they propose acts as a  
 reservoir of catalytically active species for the asymmetric epoxidation.

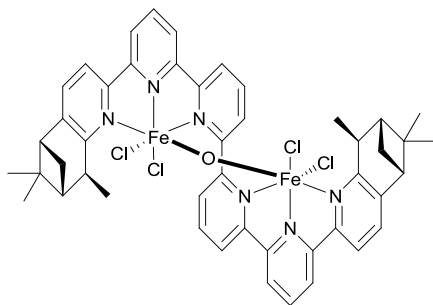
Numerous reports of epoxidation effected by metal complexes with non-salen  
 ligands also emerged in 2008. The Yamamoto group has reported a vanadium-  
 285 catalysed enantioselective desymmetrisation of *meso* secondary allylic and  
 homoallylic alcohols that employs  $C_2$ -symmetric bis(hydroxamic acid) ligands in  
 conjunction with vanadium(V) (Scheme 17).<sup>40</sup> Notably, good e.e.s are obtained even  
 with *cis*-disubstituted olefins, in contrast to Sharpless Ti-tartrate systems.



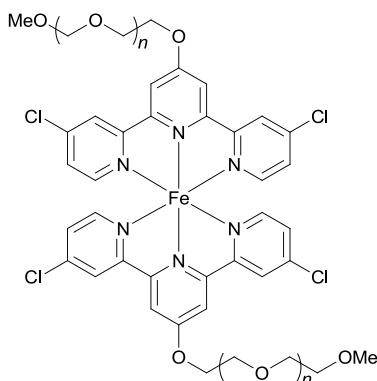
**Scheme 17**

Brückner has also examined such desymmetrisations, employing both Ti(IV)-  
 290 tartrate (Sharpless) and Zr(IV)-tartrate catalytic systems.<sup>41</sup> Sharpless conditions  
 furnished *anti*-configured monoepoxides, but when zirconium was employed, the  
 stereocomplementary *syn*-configured monoepoxides were formed instead, potentially  
 a transformation of great synthetic utility. The authors have also studied the  
 295 relationship between e.e. and reaction time and present evidence to support a  
 scenario of e.e. enhancement with time as a result of preferential overoxidation of  
 the minor enantiomer.

Other complexes reported in 2008 for metal catalysed epoxidation include Mn(porphyrinato) systems disclosed by Mohajer<sup>42</sup> and Rayati,<sup>43</sup> as well as a tripodal *N*-capped tris(oxo)amino Fe(III) system disclosed by Dilworth and Pascu.<sup>44</sup> Saladino and Crucianelli have used adducts derived from MeReO<sub>3</sub> and homochiral amines to effect epoxidation with urea-hydrogen peroxide as primary oxidant; e.e. values were modest, but were observed to improve when the catalysts were microencapsulated in polystyrene.<sup>45</sup> Similarly, Yamazaki employed MeReO<sub>3</sub> with 3-methylpyrazole for organic solvent-free epoxidation.<sup>46</sup> Two reports have appeared on pyridyl iron complexes. The Kwong group have employed a homochiral sexipyridine ligand to prepare a diiron complex that catalysed the hydrogen peroxide-mediated epoxidation of aryl alkenes with e.e. values up to 43% (Scheme 18).<sup>47</sup> The approach of Che and co-workers was to employ a (non-stereogenic) bis(terpyridine)iron system wherein the ligands were fused to PEG fragments to aid catalyst recovery and reuse.<sup>48</sup> The catalyst was able to epoxidise a wide variety of alkenes including both electron-rich and electron-poor systems with varying substitution patterns, enones and dienes; yields were consistently high (Scheme 19).



**Scheme 18**

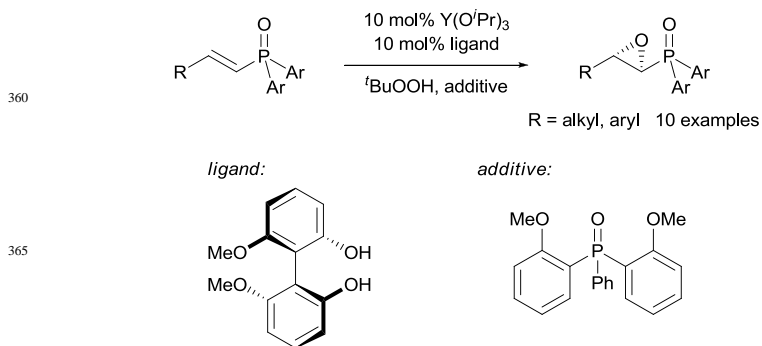


**Scheme 19**

Two reports from Beller also concern iron-based catalysts. In one, an iron catalyst system is generated *in situ* from FeCl<sub>3</sub>·6H<sub>2</sub>O, pyridine-2,6-dicarboxylic acid and substituted benzylamines.<sup>49</sup> When employed in conjunction with hydrogen peroxide, a wide variety of aliphatic and aromatic alkenes may be epoxidised in good yield; it

proved possible to vary the benzylamine substituents to optimise the yield for each substrate. In the second, related report, the catalytic system is generated from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , pyridine-2,6-dicarboxylic acid and a homochiral aminosulfonamide.<sup>50</sup> This biomimetic catalytic system, in conjunction with hydrogen peroxide, effected the epoxidation of aryl alkenes in up to 71% e.e. Mechanistic studies are detailed and a small non-linear effect is described, implying the participation of several chiral iron complexes in catalysing the reaction.

A significant disclosure from Shibasaki concerns the development of a system for the catalytic epoxidation of a specific, unusual substrate class, namely  $\alpha,\beta$ -unsaturated phosphine oxides.<sup>51</sup> The optimal catalyst is derived from  $\text{Y}(\text{O}^i\text{Pr})_3$  and an axially chiral biaryl diol, and e.e. values up to 98% have been obtained (Scheme 20).



**Scheme 20**

Several reports in 2008 concern ligand-free metal-catalysed alkene epoxidation. Linic has demonstrated that a silver nanowire can catalyse ethylene epoxidation by  $\text{O}_2$  and has demonstrated that the  $\text{Ag}(100)$  surface facet is most effective for minimising competing C-C bond cleavage in this transformation.<sup>52</sup> Silver was also employed by Chen and co-workers for the production of a magnetically-recyclable nanocomposite effective at catalysing the *tert*-butyl hydroperoxide-mediated epoxidation of styrene.<sup>53</sup> Wong reports the use of  $\text{Mn}(\text{ClO}_4)_2$  with peracetic acid for terminal aliphatic alkene substrates<sup>54</sup> and Bhattacharyya reports the use of oxo-diperoxo-Mo(VI) complexes with hydrogen peroxide.<sup>55</sup>

Some progress in the field of electrochemically-mediated epoxidation has been made in 2008. Page and Marken report the use of iminium catalysts (including that shown in Scheme 5), in conjunction with electrochemically-generated oxidants, to effect asymmetric alkene epoxidation.<sup>56</sup> Their approach employs the recently developed boron-doped diamond electrode for the direct generation of peroxo intermediates from water. Electrochemically-generated persulfate affords comparable e.e. values to those obtained with commercially available persulfate as oxidant. Percarbonate also proved to be a successful electrochemically-generated oxidant; its use with iminium salts to effect alkene epoxidation has not previously been reported. Another report, from Bouet, concerns the electrochemical generation of high-valent salen-Mn-oxo intermediates for stilbene epoxidation.<sup>57</sup>

Other miscellaneous, noteworthy disclosures include Chmielewski's report of glycosyl hydroperoxides as stereoselective stoichiometric oxidants for epoxidation of enones and quinones, for which e.e. values up to 95% are observed.<sup>58</sup> Similarly,

Oh has employed homochiral tertiary amine-*N*-oxides (strychnine *N*-oxide, brucine *N*-oxide and 17-oxosparteine *N*-oxide) as stereoselective stoichiometric oxidants for epoxidation of chalcones, achieving e.e. values up to 82%.<sup>59</sup> Bakó has reported an asymmetric phase-transfer mediated epoxidation of chalcone catalysed by homochiral crown ethers derived from monosaccharides, which proceeds with up to 94% e.e.<sup>60</sup> Finally, the Rablen group have reported a comprehensive DFT study of the origins of stereoselectivity in the epoxidation of carene by performic acid.<sup>61</sup>

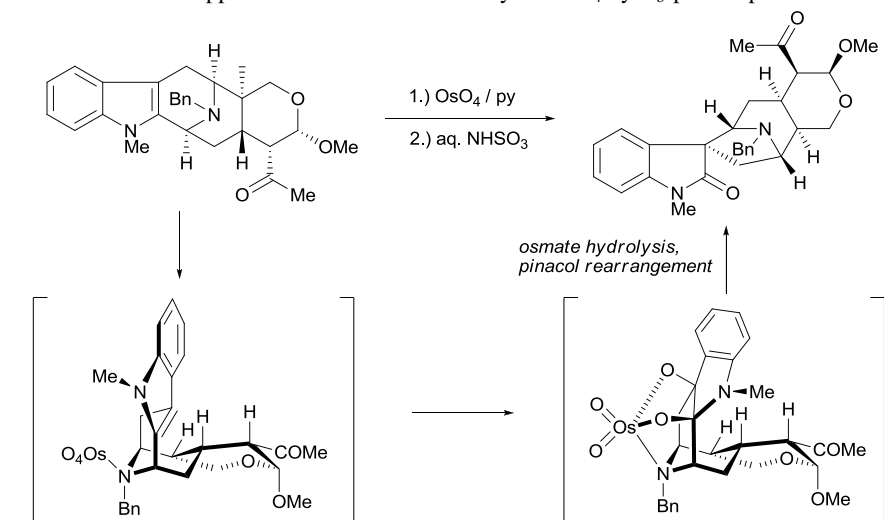
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## 1.2 Alkene dihydroxylation

Several reviews have appeared in 2008 concerning various aspects of alkene dihydroxylation, from Christie<sup>62</sup> (contrasting Os and Pd for dihydroxylation and aminohydroxylation), Haudrechy<sup>63</sup> (osmylation regioselectivity), Pitts<sup>64</sup> (Os encapsulation, microwave acceleration) and Salvador<sup>65</sup> (dihydroxylation of steroids).

Osmium-mediated asymmetric dihydroxylation remains an active area of research. Branco, Crespo, Afonso and co-workers have reported an attempt to render the Sharpless AD reaction more environmentally benign by employing a water-surfactant medium.<sup>66</sup> They report comparable yields and enantioselectivities for a variety of substrates when compared to water-*tert*-butanol solvent systems and have demonstrated effective recovery and reuse of the active catalyst by nanofiltration. Use of environmentally benign hydrogen peroxide as terminal oxidant is also desirable and a recent development in this area is due to Richardson, who has reported oxidation of *N*-methylmorpholine to the *N*-oxide (which in turn reoxidises the Os<sup>VI</sup>) by hydrogen peroxide, catalysed by carbon dioxide.<sup>67</sup>

Perisamy has reported a mechanistic study relating the electronic character of *trans*-stilbenes to the observed e.e. values for their dihydroxylation.<sup>68</sup> An interesting example of indole dihydroxylation in total synthesis has been disclosed by Cook, who presents a detailed mechanistic study on a substrate-controlled osmylation in the context of the total synthesis of (+)-alstonisine (Scheme 21).<sup>69</sup> Evidence is described that supports intramolecular delivery of OsO<sub>4</sub> by N<sub>b</sub>-precomplexation.

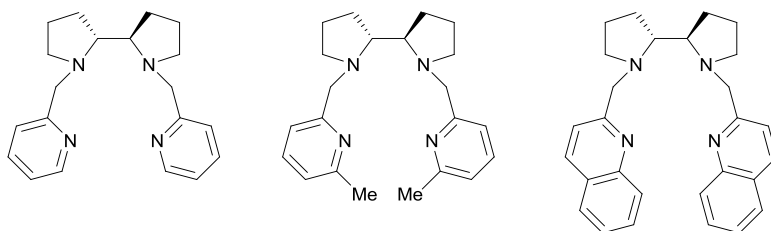


Scheme 21

Two reports concern cinchona AD ligand immobilisation. The Fenniri group have employed TentaGel-supported (DHQ)<sub>2</sub>PHAL ligands.<sup>70</sup> This permitted easy recycling and e.e. values were comparable with solution phase for some (but not all) substrates. In contrast, the Cha group have pursued copolymerisation of derivatised AD ligands with various monomers; in one instance a polymethylmethacrylate copolymer afforded good e.e. values, but activity varied for different substrates.<sup>71</sup>

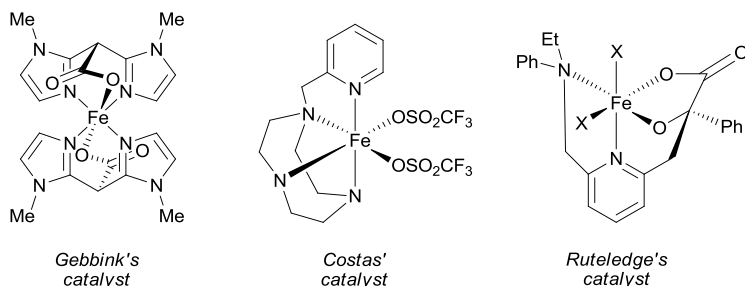
Two disclosures on Os-mediated dihydroxylation do not concern asymmetric induction. Lee and Lee have reported dihydroxylation catalysed by a polystyrene-imidazolium resin-supported Os complex<sup>72</sup> and Fache has reported an unexpected and potentially synthetically useful simultaneous Os-mediated dihydroxylation/tosyl group removal.<sup>73</sup>

In addition to osmium-based systems, numerous reports on iron-based systems continue to appear, due to its vastly lower cost and toxicity. A significant disclosure from Que and co-workers concerns their recent attempts to develop biomimetic iron complexes for asymmetric alkene dihydroxylation.<sup>74</sup> They report three tetracoordinate C<sub>2</sub>-symmetric ligands (Scheme 22), which when complexed to Fe<sup>II</sup> are able to catalyse the hydrogen peroxide-mediated dihydroxylation of alkenes with up to 97% e.e., although stereoselectivity is highly substrate-dependent, with *cis*-disubstituted and aryl alkenes giving markedly lower e.e. values.



**Scheme 22**

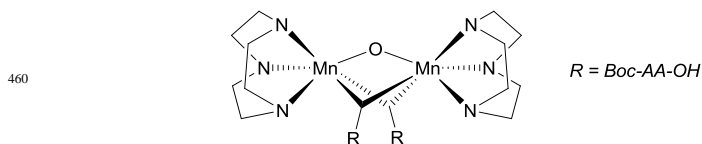
Three other reports also concern catalytic iron complexes inspired by non-heme Rieske dioxygenases. Gebbink has developed a bis(methylimidazolyl)propionate ligand,<sup>75</sup> Costas has employed a pyridyltriazacyclononane ligand<sup>76</sup> and Ruteledge has described a peptidomimetic pyridylcarboxylate ligand. The corresponding Fe<sup>II</sup> complexes are shown in Scheme 23. All are able to effect dihydroxylation of alkene substrates with varying activity and selectivity, although asymmetric induction has not yet been investigated. A DFT theoretical study of non-heme iron catalysis of alkene dihydroxylation has also been reported by Comba.<sup>77</sup>



**Scheme 23**

As regards other metals, Feringa has, in two reports, detailed dinuclear

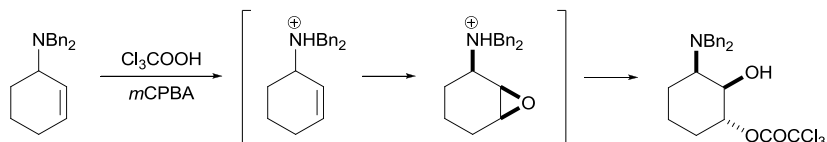
manganese complexes that effect alkene dihydroxylation (Scheme 24). The first concerns the mechanism of the reaction and the role played by additives.<sup>78</sup> The second concerns the use of homochiral *N*-protected amino acids as bridging ligands in such complexes and reports the first successful manganese-based system for catalytic asymmetric alkene dihydroxylation, albeit with modest e.e. values.<sup>79</sup>



**Scheme 24**

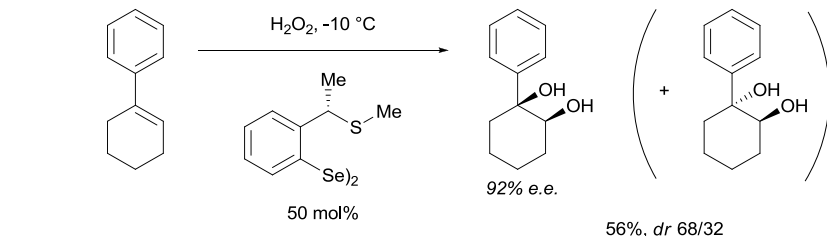
Other reports of metal-mediated alkene dihydroxylation include the use of a molybdenum acetylide by Umbarkar,<sup>80</sup> a ruthenium triazacyclononane system by Che<sup>81</sup> and methodology reported by Plietker that utilises ruthenium tetroxide as oxidant, employing a camphorsultam chiral auxiliary for substrate control of alkene dihydroxylation, proceeding in up to 99% e.e.<sup>82</sup>

In the area of metal-free alkene dihydroxylation, a noteworthy disclosure from the Davies group, in the form of two reports published simultaneously, concerns the dihydroxylation of 3-aminocyclohexene and *N*-substituted analogues thereof.<sup>83</sup> They report a protocol that employs a peracid under strongly acidic conditions to furnish the 1,2-*anti*-2,3-*syn* product with high diastereoselectivity. Protonation of the amino functionality is believed not only to suppress *N*-oxide formation, but also to ensure hydrogen bonding with the oxidant and epoxidation with high facial selectivity; *trans*-diaxial epoxide opening then ensues (Scheme 25).



**Scheme 25**

Selenium-catalysed dihydroxylation has been the subject of two reports by Santi, who details a catalytic system based on diphenyldiselenide in conjunction with stoichiometric hydrogen peroxide.<sup>84</sup> Both aryl and alkyl olefins are dihydroxylated in good yield, although both *syn* and *anti* diols are formed, the ratio being dependent on the substrate. Interestingly, a preliminary attempt at asymmetric induction is also described, employing a diphenyldiselenide possessing an *ortho*-substituent with an  $\alpha$ -stereocentre (Scheme 26). An e.e. of 92% was obtained for dihydroxylation of 1-phenylcyclohexene, but both d.r. and overall yield were modest.

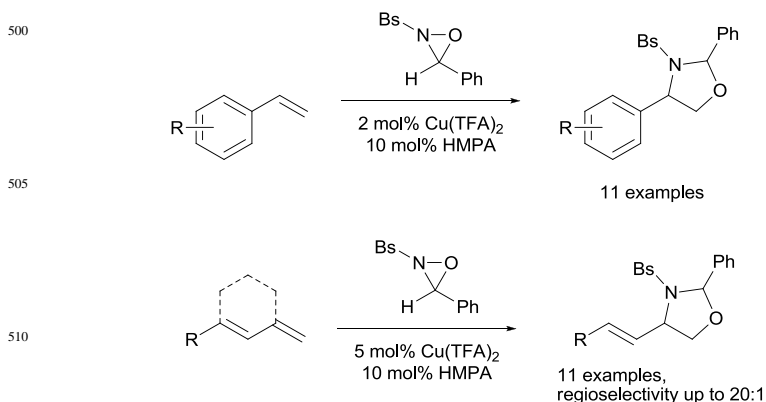


**Scheme 26**



### 1.3 Alkene aminohydroxylation

An important disclosure in 2008 came from the Yoon group, who gave a full report on their development of a widely-applicable copper-catalysed aminohydroxylation reaction (Scheme 27).<sup>85</sup> The reaction employs *N*-sulfonyloxaziridines, more commonly associated with epoxidation and other oxygen transfer reactions; a mechanistic rationale is given for the catalyst-induced alternative reaction pathway observed in this instance. The conditions have been optimised for styrenes and 1,3-dienes, with excellent regioselectivity being observed for many dienes. The oxazolidine product may be ring-opened to the corresponding amino alcohol under acidic conditions and several useful further transformations are demonstrated. In a separate disclosure, the Yoon group have shown that a different transition metal catalyst can afford the isomeric isoxazolidine products.<sup>86</sup>



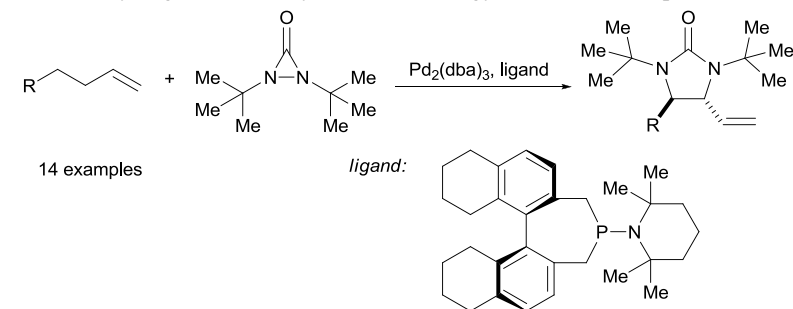
**Scheme 27**

The McLeod group have reported their studies on the regioselectivity of Sharpless asymmetric aminohydroxylation of various functionalised pent-2-enoic esters, which are precursors to various aminosugars.<sup>87</sup> They offer a rationale for the inversion of regiochemistry seen for these substrates upon switching from phthalazine (PHAL) to anthraquinone (AQN) ligands. The Davies group have previously developed methodology for the synthesis of *anti*- $\alpha$ -hydroxy- $\beta$ -amino esters by a two-step aminohydroxylation of the corresponding acrylates. In 2008 they used this methodology in the total syntheses of xestoaminol C, sphinganine and sphingosine.<sup>88</sup>

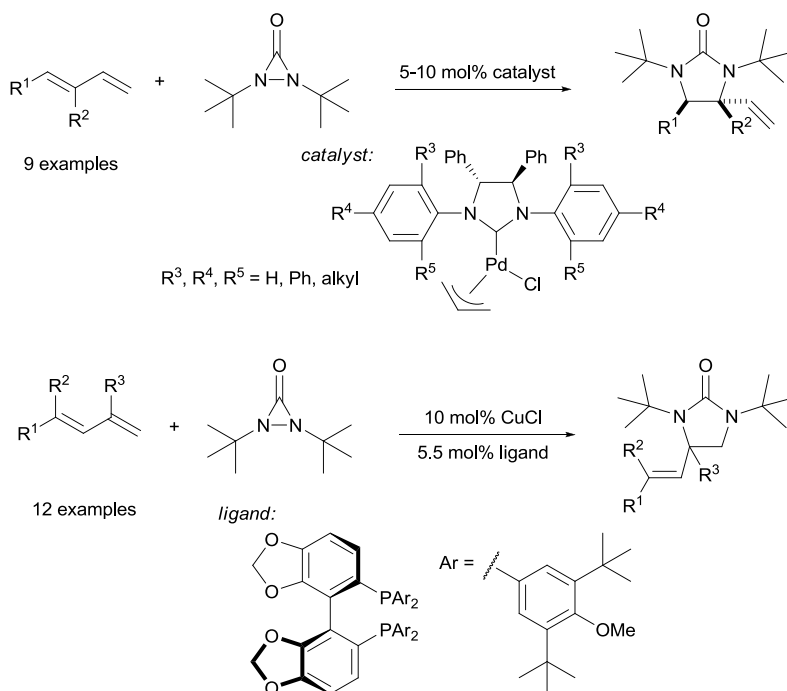
### 1.4 Alkene diamination

Sigman has recently reviewed palladium-catalysed alkene difunctionalisation, including alkene diamination.<sup>89</sup> Both the Shi and Muñiz groups have been very active in this area in 2008. The Shi group have continued to develop their methodology employing di-*tert*-butyldiaziridinone and have reported the catalytic asymmetric allylic and homoallylic diamination of terminal olefins (Scheme 28).<sup>90</sup> Cleavage of the imidazolidinone ring in the products may be effected under strongly acidic conditions, affording the corresponding vicinal diamines. Stereoinduction is good, with e.e. values generally >90% and in one instance 99% e.e. was obtained for a bifunctional substrate. In related work, the group have effected the diamination of

dienes, employing both a Pd<sup>0</sup> catalyst<sup>91</sup> (up to 91% e.e.) and a Cu<sup>I</sup> catalyst<sup>92</sup> (up to 74% e.e.). The two catalytic systems enjoy a nice degree of complementarity in  
 535 terms of regioselectivity, with the copper catalyst favouring diamination of the less substituted alkene and the palladium catalyst favouring the more substituted alkene (Scheme 29). Cycloguanidation by this methodology has also been reported.<sup>93</sup>

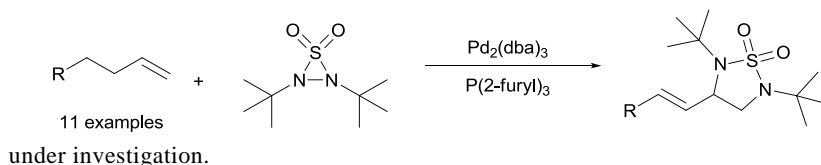


**Scheme 28**



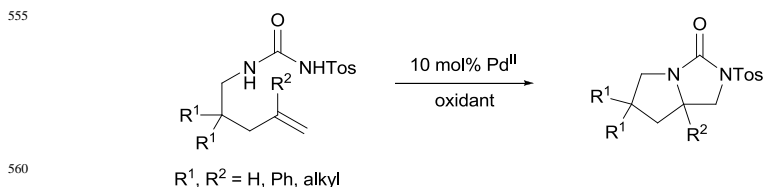
**Scheme 29**

The Shi group have also published a preliminary communication concerning diamination with *N,N*-di-*tert*-butylthiadiaziridine-1,1-dioxide which, proceeds *via* a distinct mechanism to that which operates for di-*tert*-butyldiaziridinone; the  
 545 regiochemical outcome is also different (Scheme 30)<sup>94</sup>. The mechanism is discussed and the authors state that an asymmetric variant of this transformation is currently



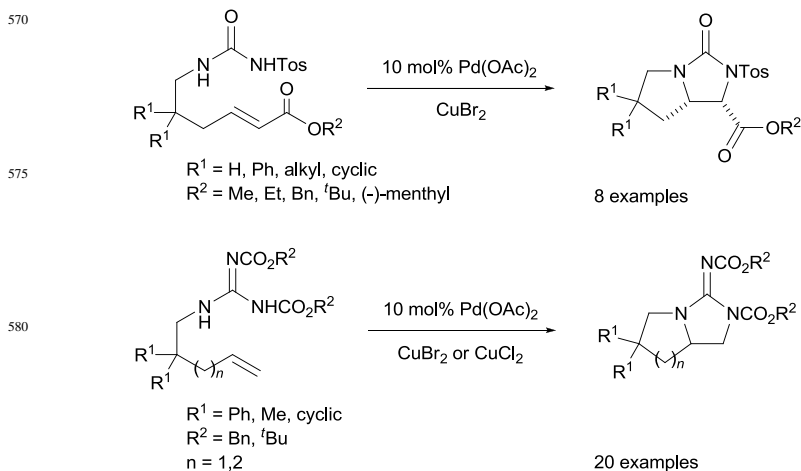
**Scheme 30**

The Muñiz group have reported several advances in their development of methodology for intramolecular diamination with tethered *N*-sulfonylureas. The key transformation is outlined in Scheme 31, and Muñiz has published an in-depth study<sup>95</sup> with PhI(OAc)<sub>2</sub> as oxidant, employing NMR titration, kinetic and competition experiments and isotopic labelling for mechanistic elucidation; evidence for Pd<sup>IV</sup> intermediates is presented.



**Scheme 31**

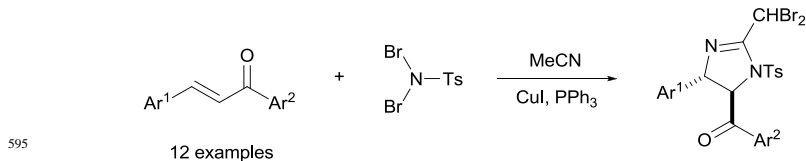
In a separate publication, Muñiz and Barluenga examine the importance of halogenated intermediates in the case of other stoichiometric oxidant(s), namely copper(II)bromide. Also, the transformation may be effected with a source of electrophilic iodine; in this (palladium-free) case, a distinct mechanism involving an iodonium intermediate is operative.<sup>96</sup> Also in 2008, Muñiz has expanded the scope of the transformation to include diamination of acrylate esters<sup>97</sup> and also to effect cycloguanidation<sup>98</sup> (Scheme 32).



**Scheme 32**

Several other reports merit attention: Pan and Li have reported an unusual

catalytic diamination of chalcones using *N,N*-dibromo-*p*-toluenesulfonamide as electrophile and nitriles as nucleophiles.<sup>99</sup> The reaction employs copper(I)iodide and triphenylphosphine as catalyst, and acetonitrile as both solvent and nucleophile  
590 (Scheme 33).

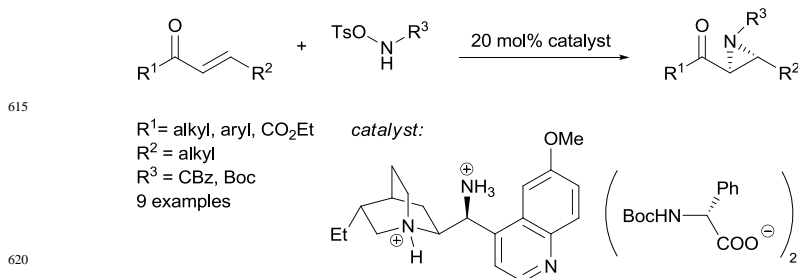


**Scheme 33**

Lloyd-Jones and Booker-Milburn have reported previously on palladium(II)-catalysed alkene diamination, and in 2008 have extended this methodology to encompass oxidative alkene carboamination as well.<sup>100</sup> Finally, M. Li and co-  
600 workers have reported a DFT theoretical study on the palladium(II)-catalysed intermolecular 1,2-diamination of conjugated dienes.<sup>101</sup>

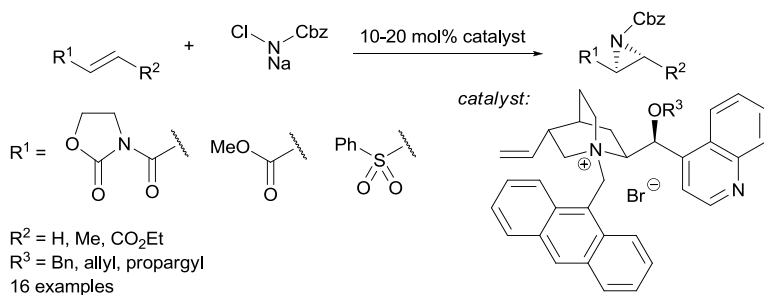
### 1.5 Alkene aziridination

2008 has seen the publication of a review on the aziridination of  $\alpha,\beta$ -unsaturated  
605 enones.<sup>102</sup> A significant development in this specific area was also communicated by Melchiorre and co-workers, who have described an organocatalytic asymmetric aziridination of  $\alpha,\beta$ -unsaturated enones that has wide applicability and gives good stereoselectivity.<sup>103</sup> The transformation employs an unusual primary ammonium salt catalyst possessing stereocentres in both the cation and anion (Scheme 34). Good to  
610 excellent e.e. values (up to 99%) are achieved, although selectivity can drop with an aryl substituent on the enone  $\beta$  position.



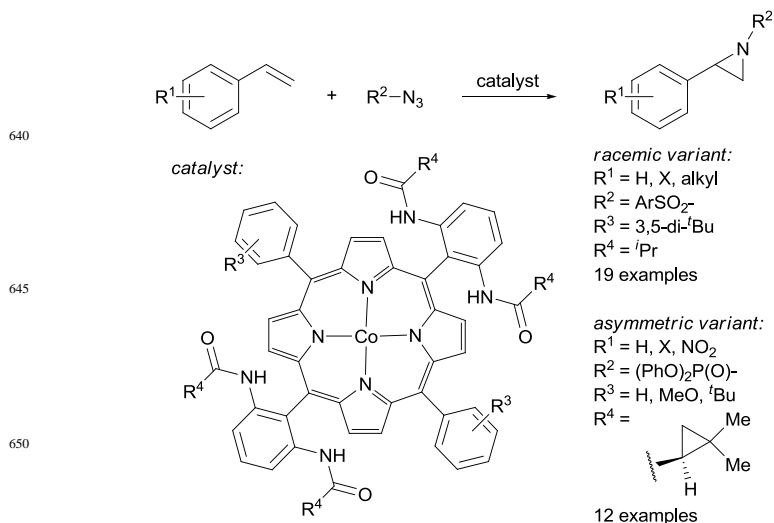
**Scheme 34**

Minakata has also addressed the asymmetric aziridination of electron-deficient olefins, namely  $\alpha,\beta$ -unsaturated esters, sulfones and *N*-acyloxazolidinones.<sup>104</sup> In this  
625 instance a cinchona-derived ammonium salt with an achiral anion was employed; e.e. values up to 87% were observed (Scheme 35). Zhang has employed cobalt porphyrins to effect alkene aziridination and in 2008 published both an initial communication on a non-asymmetric system<sup>105</sup> and a full article on an asymmetric variant.<sup>106</sup> As shown in Scheme 36, various nitrene sources have been employed and  
630 a cyclopropyl stereocentre is used to induce asymmetry. Yields are high for the non-asymmetric variant; moderate to good e.e. values (up to 71%) have been obtained with the homochiral porphyrin, but at the expense of yield. Cenini has also reported



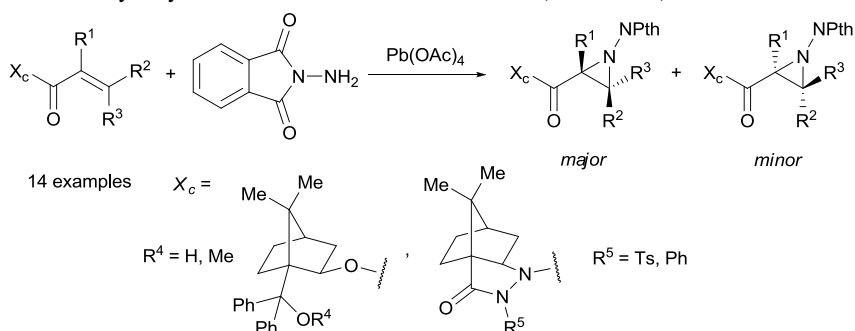
studies on cobalt porphyrin-catalysed aziridination.<sup>107</sup>

**Scheme 35**



**Scheme 36**

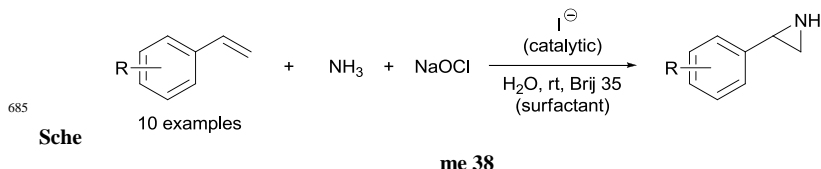
Elsewhere, two reports concern induction of asymmetry by means of chiral auxiliaries. Chen has used various camphor-derived auxiliaries to effect aziridination of  $\alpha,\beta$ -unsaturated esters and hydrazides, with *N*-aminophthalimide and lead tetraacetate as oxidant.<sup>108</sup> Diastereomeric ratios >95:5 are reported, and cleavage of the auxiliary may be effected under basic conditions (Scheme 37).



### Scheme 37

Dabbagh has taken the approach of attaching a chiral auxiliary to a nitrene source and has reported an intriguing BINOL-based imidoyl azide for this purpose.<sup>109</sup> No notable stereoselection was observed in aziridination, but this conceptually distinct approach may yet be useful with further optimisation. O'Brien has explored substrate control in the diastereoselective aziridination of cyclic allylic alcohols with various chloramine salts.<sup>110</sup> *Cis*-hydroxyaziridines predominated, with *cis/trans* ratios influenced by choice of chloramine salt. In one specific instance (1-substituted cyclopent-2-en-1-ols), epoxy sulfonamide products were formed as opposed to aziridines. Substrate control also underlies the work of the Liu group, who have communicated their work on the intramolecular aziridination of glycals.<sup>111</sup> Tethered sulfonamides have been employed, undergoing rhodium-catalysed oxidation by hypervalent iodine reagents, with the nitrenes so generated effecting aziridination in a stereodefined manner; subsequent nucleophilic ring-opening allows access to aminoglycosides. DFT theoretical studies are also outlined.

In the field of non-asymmetric alkene aziridination, a major disclosure has come from De Vos and Sels, who describe the first direct catalytic aziridination of styrenes with ammonia, obviating the need for protecting groups.<sup>112</sup> The reaction employs sodium chlorate as oxidant and iodide ions as catalyst in a micellar system achieving yields of 30-92% (Scheme 38). The use of a cheap oxidant, atom efficient nitrogen source, environmentally benign aqueous medium and mild conditions (ambient temperature) render this transformation likely to be widely adopted; the authors are currently determining the substrate scope of this reaction.

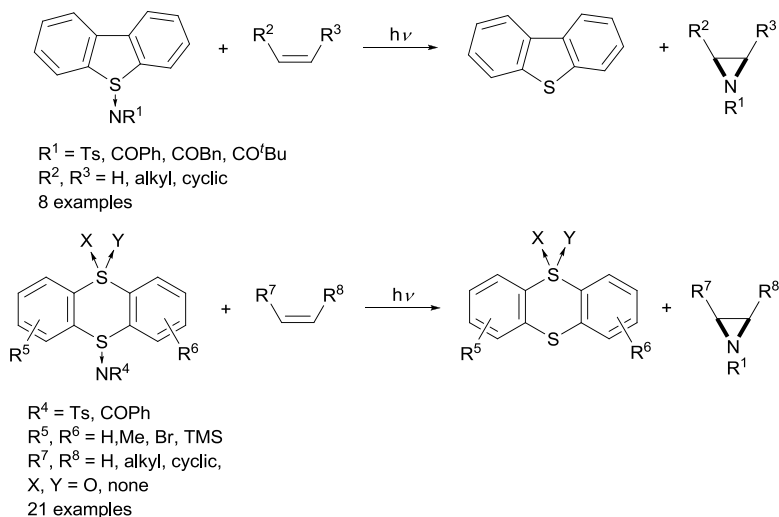


Several other reports on metal-free alkene aziridination appeared in 2008. Butkevitch employed a bicyclic *N*-aminoimide as nitrene source,<sup>113</sup> and Fan and Wang have reported mild conditions for hypervalent iodine-mediated aziridination with *p*-toluenesulfonamide.<sup>114</sup> Fu and Guo have reported a triflic acid-promoted aziridination of electron-deficient olefins by aliphatic azides, and have undertaken a DFT theoretical study to permit elucidation of mechanism and to rationalise a correlation between olefin basicity and reaction yield.<sup>115</sup> Morita has employed an unusual method of nitrene generation, namely photolysis of sulfilimines.<sup>116</sup> *In situ* trapping with alkenes leads to the corresponding aziridines as shown in Scheme 39.

Amongst reports on metal-catalysed non-asymmetric aziridination, copper dominates. Appella has reported hypervalent iodine-induced aziridination of terminal aliphatic alkenes with sulfonamides, catalysed by a copper *N*-heterocyclic carbene complex.<sup>117</sup> Kühn has reported a catalytic copper complex with an unusual perfluoroalkoxyaluminate counteranion,<sup>118</sup> and Comba has disclosed an experimental and theoretical study of the catalytic activity of various copper(bispidine) complexes.<sup>119</sup> Pyridyl ligands have been employed by both Hirotsu<sup>120</sup> (who reports a copper thiocalix[3]pyridine complex) and Kim and Chang<sup>121</sup> (who report use of a chelating 2-pyridylsulfonyl ligand).

Group 8 metals have also been employed – Gallo describes a heterogenised

ruthenium porphyrin catalyst<sup>122</sup> and Che's iron bis(terpyridine) complex, described in Section 1.1 (Scheme 19) for epoxidation, is also reported to effect aziridination.<sup>48</sup> Finally, Bolm has reported the catalytic activity of iron(II)triflate in the  
 710 iminoiodanine-mediated aziridination of styrenes<sup>123</sup> and silyl enol ethers,<sup>124</sup> which hydrolyse upon workup to give  $\alpha$ -amino ketones. In the former instance, the



accelerating effect of ionic liquid additives is described.

**Scheme 39**

## 715 1.6 Alcohol oxidation

2008 has seen continued activity in the field of aerobic alcohol oxidation, such is the desirability of systems that utilise molecular oxygen as terminal oxidant. A highly noteworthy advance in this area is that due to Liang,<sup>125</sup> who has reported a metal-free aerobic oxidation of primary and secondary alcohols (aryl and alkyl) to the  
 720 corresponding carbonyl compounds. The reaction employs a catalytic mixture of TEMPO,  $\text{NaNO}_2$  and HCl. The oxidation proceeds at ambient temperature and, crucially, at atmospheric pressure of  $\text{O}_2$ , in contrast to previously reported work. The authors note the low cost of the constituents of the catalytic system and point out that the absence of metal catalysts removes concerns over metal contaminants in the  
 725 products.

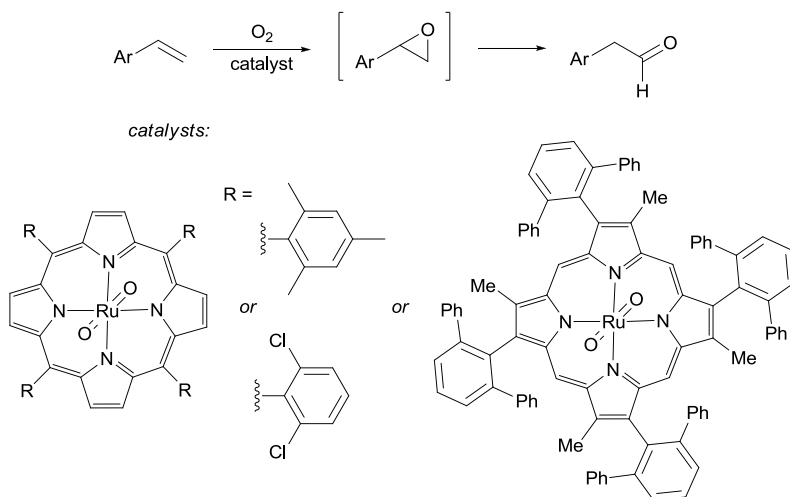
Concerning metal-catalysed aerobic oxidations, the Ison group have communicated their investigations into the mechanism of an  $\text{Ir}^{\text{III}}$ -catalysed aerobic oxidation of primary and secondary alcohols.<sup>126</sup> The proposed mechanism is one in which iridium remains in the +3 oxidation state throughout the catalytic cycle. An  
 730 advantage of this iridium-based system is that it does not exhibit any tendency to precipitate bulk metal due to catalyst decomposition, a problem that plagues certain analogous palladium-mediated aerobic oxidations.

Palladium-mediated aerobic alcohol oxidation continues to develop, with Sun reporting a new class of sulfonated  $\alpha$ -diimine ligands for this transformation<sup>127</sup> and  
 735 Shimazu reporting palladium alkylamine complexes that exhibit good catalytic efficiency.<sup>128</sup> Aerobic palladium oxidation has been employed for specific synthetic

purposes by Gozzi and Fache who report tandem one-pot allyl alcohol oxidation–Heck reactions,<sup>129</sup> and by Stoltz, who reports the use of palladium-mediated oxidative kinetic resolution methodology, developed previously, in the context of alkaloid total synthesis.<sup>130</sup> Other metals have also been employed for catalysis of aerobic alcohol oxidation in 2008, such as gallium–aluminium mixed-oxide-supported gold nanoparticles reported by Cao,<sup>131</sup> and copper nanocomposites reported by Pal.<sup>132</sup>

## 1.7 Other oxidations

Che and co-workers have described a ruthenium porphyrin-catalysed oxidation of terminal aryl alkenes to aldehydes.<sup>133</sup> This transformation is of particular note, since it employs air as the sole terminal oxidant. Under comparable aerobic conditions, the Pd<sup>II</sup> or Cu<sup>II</sup>-mediated Wacker oxidation typically furnishes methyl ketones, thus Che's method represents a useful reversal of regioselectivity. The reaction proceeds by epoxidation and subsequent *in situ* rearrangement (Scheme 40).



**Scheme 40**

Other significant advances in oxidation methodology in 2008 include Kita's report of a chiral hypervalent iodine reagent for the enantioselective dearomatisation of phenols,<sup>134</sup> Liu's report of a palladium-catalysed intermolecular aerobic oxidative amination of terminal alkenes<sup>135</sup> and Katsuki's reports on asymmetric sulfide oxidation catalysed by aluminium(salalen)<sup>136</sup> and iron(salan).<sup>137</sup> Also of importance are Donohoe's report on the use of pyridine-*N*-oxide as an alternative re-oxidant for osmium-catalysed oxidative cyclisation,<sup>138</sup> and several reports from the Williams group further developing their "borrowing hydrogen" methodology, employing one pot tandem dehydrogenation/hydrogenation sequences to effect diverse functional group interconversions.<sup>139</sup> Barrett has disclosed mechanistic studies on benzylic oxidations catalysed by Bi<sup>III</sup> salts.<sup>140</sup>

Mention should also be made of continued progress in the field of biooxidation. Boyd has continued to publish extensively on enzymatic arene dihydroxylation, with specific highlights in 2008 including use of substrates such as 2-naphthyl (in



conjunction with Gawronski),<sup>141</sup> mono- and tricyclic azaarene,<sup>142</sup> 2,2'-bipyridyl,<sup>143</sup> and 4,4'-bipyridyl<sup>144</sup> (in conjunction with James) and methyl benzoates.<sup>145</sup>

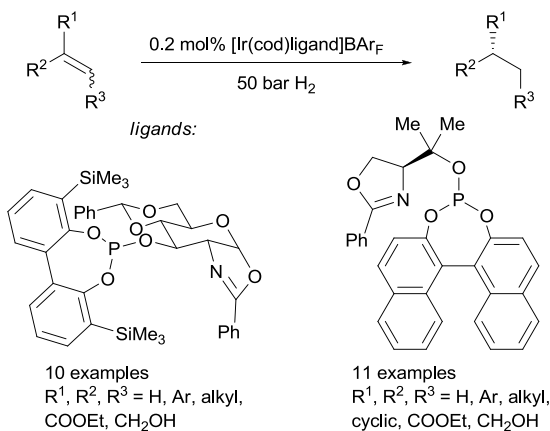
Finally, Que and Tolman have published a concise review on biologically inspired oxidation catalysts,<sup>146</sup> Rossi has reviewed selective gold-catalysed oxidation,<sup>147</sup> Murahashi has reviewed ruthenium-catalysed biomimetic oxidation,<sup>148</sup> and Punniyamurthy has reviewed copper-catalysed oxidation.<sup>149</sup>

## 2. Reduction reactions

### 2.1 Alkene hydrogenation

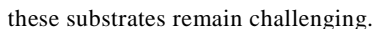
Reviews published in 2008 relevant to alkene hydrogenation include those from Andersson<sup>150</sup> (iridium-catalysed hydrogenation of alkenes with "nontraditional" substituents) and Eberhart<sup>151</sup> (BINOL-derived phosphoramidites).

The Andersson group have continued their prolific output in the field of iridium-catalysed asymmetric alkene reduction. In two separate disclosures (work undertaken in collaboration with Diéguez), they describe new biaryl phosphite-oxazoline ligands, their use in formation of iridium complexes and use of said complexes for asymmetric hydrogenation of di- and trisubstituted styrenes and stilbenes. In the first instance<sup>152</sup>, the oxazolidines are pyranoside-derived; in the second instance<sup>153</sup> they are hydroxylaminoacid-derived (Scheme 41, most active catalyst shown in each series). In both instances, excellent yields and e.e. values (>99% in some cases) are achieved with low catalyst loadings (0.2 mol% iridium).

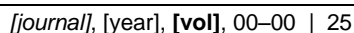


**Scheme 41**

Aside from oxazolidine ligands, the Andersson group have also published full papers on annelated thiazole<sup>154</sup> and imidazole<sup>155</sup> *N,P* ligands for alkene hydrogenation (Scheme 42). The ligands have been evaluated in the iridium-catalysed asymmetric hydrogenation of a wide variety of substituted alkenes and afford good to excellent e.e. values. In one paper,<sup>155</sup> imidazole, thiazole and oxazole ligands are contrasted and it may be seen that whilst the thiazole ligands generally afford superior e.e.s, imidazole ligands are preferred for  $\alpha,\beta$ -unsaturated ester substrates. An imidazole ligand has also been applied for the asymmetric hydrogenation of a vinyl fluoride, hitherto a difficult class of substrate for achieving

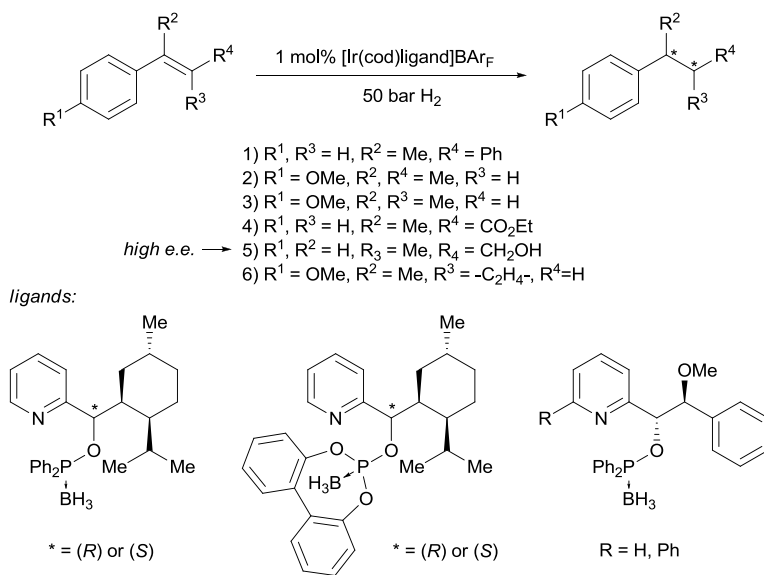


The Pfaltz group are also highly active in the iridium area and have published extensively in 2008. In one report, the group describe the synthesis of simple phosphinomethyloxazoline ligands for the iridium-catalysed asymmetric reduction of tetrasubstituted olefins (Scheme 43).<sup>156</sup> Two syntheses of the ligands are presented and four representative tetrasubstituted alkene substrates are examined, with good e.e. values (77-96%) obtained for the indene derivatives and moderate e.e. values for the acyclic case (23-67%).

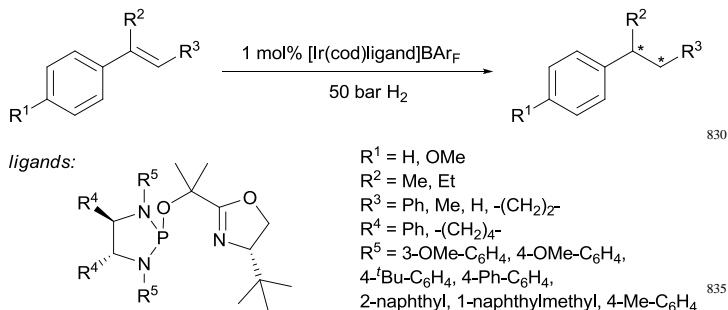


### Scheme 43

The Pfaltz group, in collaboration with the Moberg group, have also reported pyridine-phosphinite ligands derived from chiral pool materials.<sup>157</sup> These were used for asymmetric hydrogenation of a variety of trisubstituted styrenes, but in this instance e.e. values were highly substrate dependent, with good e.e. values being obtained only for the substituted cinnamyl alcohol substrate (Scheme 44). The Pfaltz group have also detailed their studies on bis(*N*-arylamino)phosphine-oxazolines as ligands for iridium-catalysed alkene reduction.<sup>158</sup> Good to excellent e.e. values were obtained for a variety of di- and trisubstituted styrenes, in contrast to the preceding report. The authors contrast these catalysts with their previously reported *N*-sulfonyl derivatives (Scheme 45, R<sup>5</sup> = SO<sub>2</sub>R) and note that the current catalysts exhibit enhanced reactivity, yet have sterically similar coordination spheres. The authors thus conclude that the altered electronic characteristics of the ligands account for the observed differences.



Scheme 44

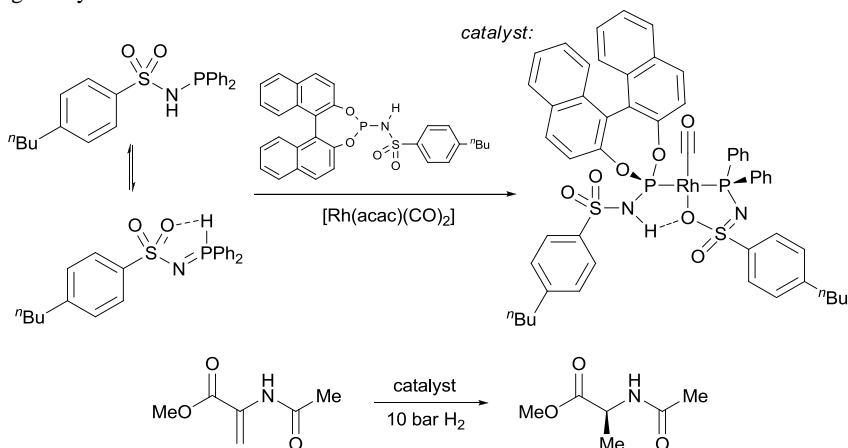


Scheme 45

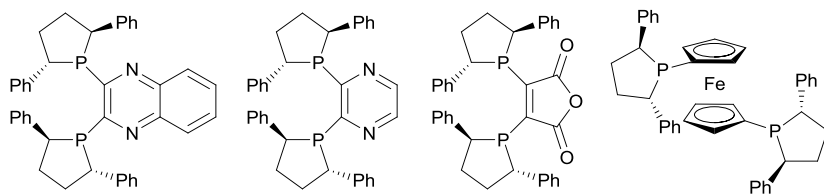
Additionally, the Pfaltz group have investigated the non-asymmetric reduction of

tri- and tetrasubstituted olefins with simple achiral PHOX (phosphino-oxazoline) ligands and have observed that iridium complexes containing such ligands are notably superior to Crabtree's catalyst for a number of substrates.<sup>159</sup> They also describe the effects of counteranion substitution and note that simply exchanging the PF<sub>6</sub><sup>-</sup> anion of Crabtree's catalyst for BArF<sup>-</sup> can dramatically increase hydrogenation yields in certain instances.

Rhodium remains the metal subject to the most attention for asymmetric alkene reduction. Amongst many new ligand systems reported in 2008, one report from Reek and co-workers is particularly noteworthy as it describes the conceptually novel approach of employing adaptive supramolecular ligands in Rh-catalysed alkene reduction.<sup>160</sup> The ligands in question, termed "METAMORPhos" ligands, were found to exist in two tautomeric forms that underwent slow exchange on the NMR timescale (Scheme 46). Upon mixing the two ligands in the presence of a rhodium source, the authors observed selective formation of the heterocomplex shown. This complex was evaluated in the asymmetric reduction of methyl 2-acetamidoacrylate (MAA) and exhibited good activity and stereoselectivity (92% e.e.). The authors studied the kinetics of hydrogenation effected with this and related catalysts and report the startling observation that for the catalyst shown, the reaction is zero-order in both substrate and hydrogen. They rationalise this unprecedented finding by proposing a new mechanism for the hydrogenation, specific to these ligand systems.



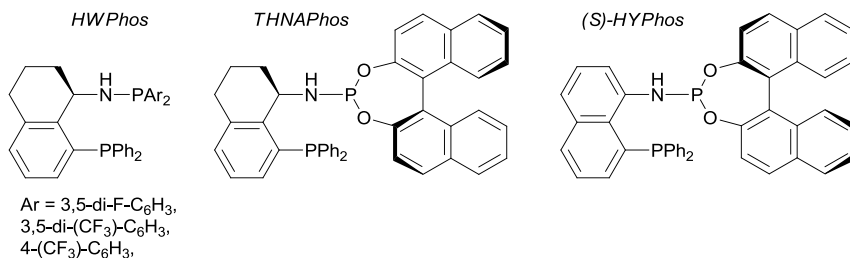
**Scheme 46**



**Scheme 47**

New phosphine ligands comprising bis-(2,5-diphenylphospholanes) with sp<sup>2</sup> carbon linkers have been reported by Fox and co-workers from Dow (Scheme 47).<sup>161</sup>

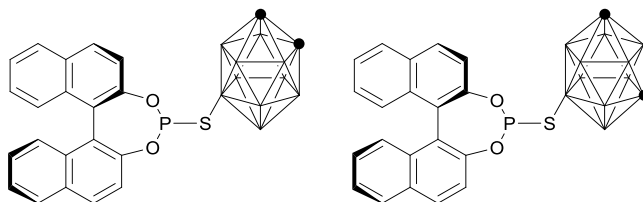
The corresponding cationic  $[Rh^I(cod)]$  complexes were prepared, and their utility in asymmetric alkene reduction was determined. The (*S,S*)-Ph-Quinox complex performed well in the reduction of itaconate (99.8% e.e.) and dehydroamino acid substrates (99.5-99.9% e.e.), and the (*S,S*)-Ph-5-Fc complex performed well for 2-substituted cinnamate substrates.



**Scheme 48**

Hu, Zheng and co-workers have described new classes of ligands based on a 1,2,3,4-tetrahydro-1-naphthylamine skeleton (Scheme 48). They have described ligands with both simple aryl groups on phosphorus<sup>162</sup> (which they have designated the “HW-Phos” family) and an axially chiral biaryl on phosphorus as a second stereochemical element (“THNAPhos”, matched case shown).<sup>163</sup> A THNAPhos-containing cationic  $Rh^I$  complex was shown to be competent at effecting the asymmetric reduction of various functionalised alkenes, specifically  $\alpha$ -dehydroamino acid esters, enamides, dimethyl itaconate and  $\alpha$ -enamido phosphonates, routinely achieving excellent e.e. values (96.7-99.9%); HWPhos-containing cationic  $Rh^I$  complexes have been evaluated for a slightly different selection of alkenes:  $\alpha$ -enolester phosphonates,  $\alpha$ -enamido phosphonates and (*Z*)- $\beta$ -(acylamino)acrylates. Also, Hu and Zheng have reported the “HY-Phos” ligand,<sup>164</sup> which is a more highly oxidised form of the THNAPhos ligand. HY-Phos performs similarly to or worse than THNAPhos for most substrate classes, with the specific exception of trisubstituted enamides, for which it is superior.

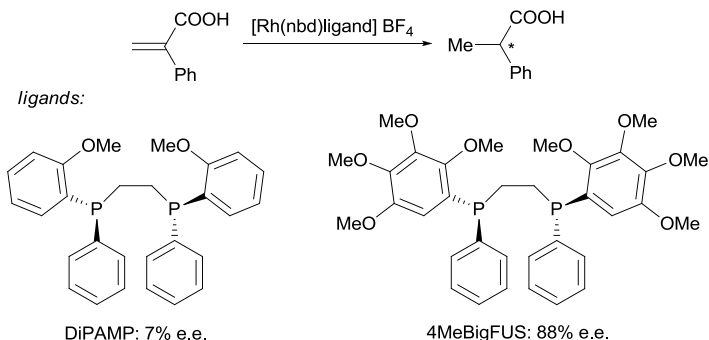
An unusual ligand class introduced by Lyubimov is carborane-containing phosphorus ligands, shown in Scheme 49.<sup>165</sup>  $Rh^I$  complexes containing these ligands have been utilised for asymmetric reduction of dimethyl itaconate (99% e.e.) and various dehydroamino acid substrates (where the best e.e. values, up to 95%, were obtained for electron-rich substrates). Another example of boron and rhodium chemistry in the reduction of alkenes was published in 2008 by Macías, who reported alkene hydrogenation on an 11-vertex rhodathiaborane.<sup>166</sup>



**Scheme 49**

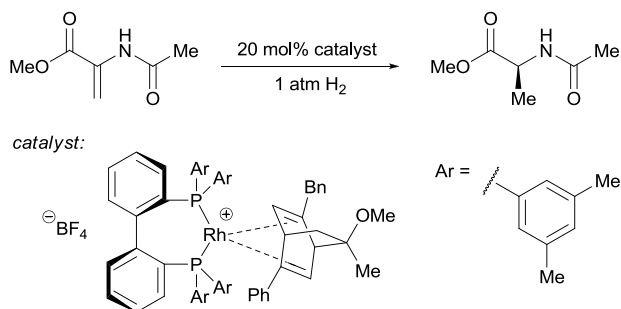
Stephan has reported an evaluation of substituted DiPAMP ligands and the stereoselection obtained when they are employed in Rh-catalysed alkene

reduction.<sup>167</sup> Numerous substrate-ligand combinations were evaluated, and it emerged that the complex containing a P-(2,3,4,5-tetra-MeO-C<sub>6</sub>H) substituted ligand ("4MeBigFUS") afforded particularly good stereoselectivity (Scheme 50).



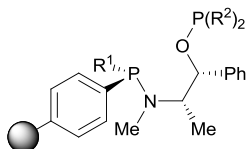
**Scheme 50**

Mikami has reported a significant synergistic effect when using the *tropos* (freely rotating) BIPHEP ligand in Rh<sup>I</sup> complexes with a homochiral diene ligand (Scheme 51).<sup>168</sup> The homochiral diene induces complete diastereocontrol in the formation of the BIPHEP Rh<sup>I</sup> complex – rotation is retarded and an additional element of stereochemistry is introduced, i.e. the BIPHEP ligand behaves as an *atropos* ligand and exhibits axial chirality in this specific complex. With this complex as catalyst, the enantioselective reduction of MAA proceeded in 91% e.e., an appreciably higher value than that obtained when using an *atropos* BINAP complex (21% e.e.).



**Scheme 51**

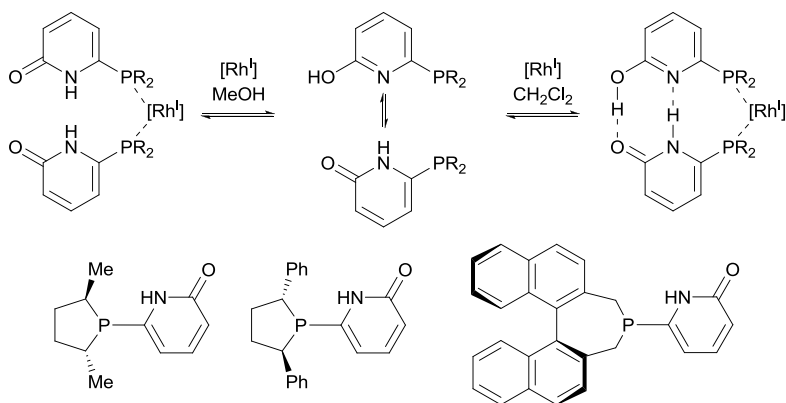
Kamer has reported the parallel synthesis and screening of polymer-supported *P*-stereogenic aminophosphane–phosphite and –phosphinite ligands (Scheme 52).<sup>169</sup> The ligands incorporate an ephedrine backbone (chiral pool material) as source of chirality, and the use of solid-phase chemistry allows for rapid ligand assembly, rhodium complex formation and catalyst screening. In the asymmetric reduction of dehydroamino acids and dimethyl itaconate, e.e. values of up to 89% were obtained.



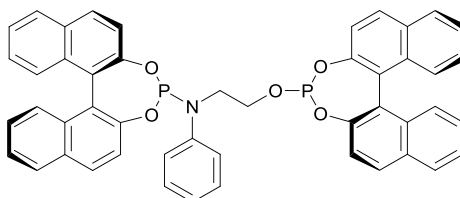
$R^1$  = ferrocenyl, *o*-anisyl, phenyl, methyl  
 $R^2$  = diphenyl, biphenol

**Scheme 52**

Börner has reported<sup>170</sup> a series of 2-pyridone-containing phosphine ligands that permit the formation of self-assembling catalysts by means of tautomerism and intramolecular hydrogen bonding in work which is conceptually related to that of Reek.<sup>160</sup> Rhodium bisphosphine complexes formed from the ligands shown in Scheme 53 enjoy extra conformational rigidity due to intramolecular hydrogen bonding as shown. In the asymmetric reduction of dehydroamino acids and dimethyl itaconate, e.e. values of up to 99% were obtained, and Börner has contrasted  $\text{CH}_2\text{Cl}_2$  and propylene carbonate as solvents. He notes that the slightly unusual choice of propylene carbonate affords higher reaction rates in several cases, in spite of the lower solubility of  $\text{H}_2$  in this solvent than in  $\text{CH}_2\text{Cl}_2$ ; this hints at a greater future role for propylene carbonate in rhodium-catalysed asymmetric alkene reduction. In a separate publication, Börner also reports, in conjunction with Kostas, a new easily accessible chiral phosphite–phosphoramidite ligand based on 2-anilinoethanol and *R*-BINOL moieties (Scheme 54).<sup>171</sup> Moderate e.e. values have been obtained using this ligand for the asymmetric reduction of dehydroamino acids and dimethyl itaconate.

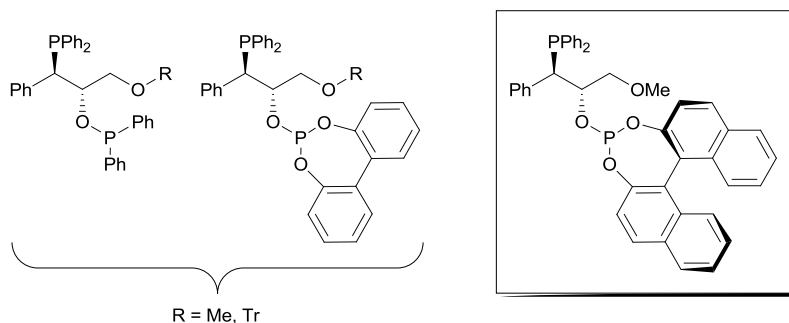


**Scheme 53**



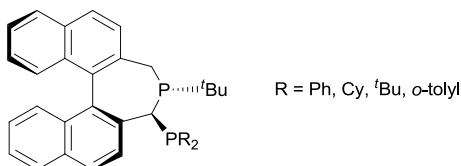
**Scheme 54**

The Vidal-Ferran group have described the preparation of a library of new *P-O-P* ligands (phosphine-phosphites and phosphinephosphinites), easily available in two synthetic steps from enantiopure Sharpless epoxy ethers.<sup>172</sup> The most selective catalyst (highlighted in Scheme 55) was formed from the ligand containing the (*S*)-BINOL motif, a case of two “matched” elements of stereochemistry – this rhodium catalyst was able to effect the asymmetric reduction of a wide variety of dehydroamino acids (both electron-rich and electron-poor), as well as dimethyl itaconate and an enol phosphate substrate, in excellent e.e.s (96-99%); an enol phosphate substrate was reduced in 92% e.e.



**Scheme 55**

Other ligands introduced in 2008 for Rh-catalysed alkene reduction include interesting BINOL derived bisphosphines reported by the Zhang group (Scheme 56).<sup>173</sup> These have been evaluated for hydrogenation of dehydro  $\alpha$ - and  $\beta$ -amino acid esters, with which they display moderate to good enantioselectivity, and for enamides, with which they display moderate enantioselectivity. Spindler and Weissenseiner have also published<sup>174</sup> a full report on WalPhos ligands that they detailed previously in preliminary form; ruthenium, rhodium and iridium complexes thereof are described for alkene and ketone reduction.



**Scheme 56**

Elsewhere in the field of rhodium-catalysed alkene hydrogenation, Heller has disclosed several detailed mechanistic studies, concerned with the transformation of precatalysts into active species,<sup>175</sup> dependence of selectivity on reactivity and concentration of intermediates,<sup>176</sup> and trinuclear rhodium complexes.<sup>177</sup> Lyubimov has reported on alkene hydrogenation in supercritical carbon dioxide, achieving good e.e. values for dimethyl itaconate reduction with simple phosphoramidite ligands (PipPhos and MorfPhos).<sup>178</sup> Grützmacher has reported a non-asymmetric alkene hydrogenation employing Rh<sup>I</sup> amides and ethanol as hydrogen donor,<sup>179</sup> and Yamamoto and Nishihara have reported<sup>180</sup> rhodium nanoclusters encapsulated with dendrimers for alkene hydrogenation.

Reports have also appeared, to a lesser degree, on the use of other metals for



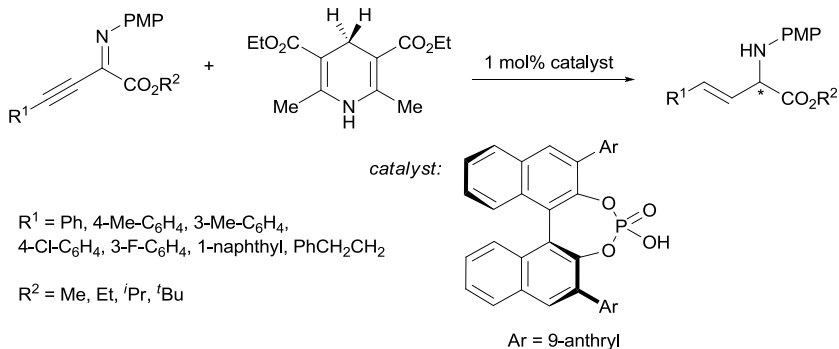
catalytic alkene hydrogenation. Preeminent amongst these in 2008 is a highly significant disclosure from Harder and co-workers, who have introduced a set of well-defined early main-group metal catalysts for the hydrogenation of a variety of conjugated alkenes.<sup>181</sup> The use of group 1 and 2 metal-based catalysts brings enormous cost advantages over transition metals. Thus far the method has only been applied to substrates with conjugated double bonds, but the exclusive mono-hydrogenation of these dienes that results could of course be synthetically desirable in certain contexts. Alkaline-earth metal catalysts are reportedly effective under relatively mild conditions (ambient temperature, 20 bar H<sub>2</sub>), whereas alkali-metal catalysts needed a far higher pressure.

Elsewhere, two reports concern ionic liquids: Yuan has described ruthenium-catalysed alkene reduction in ionic media,<sup>182</sup> and Hou has described biphasic alkene hydrogenation by functionalised ionic liquid-stabilised palladium nanoparticles.<sup>183</sup> Doctorovich has reported an interesting “hydrogen free” hydroxylamine-mediated iron-catalysed alkene reduction in aqueous media.<sup>184</sup> Also, Sajiki has described a novel palladium-on-carbon/diphenyl sulfide complex for heterogeneous alkene hydrogenation.<sup>185</sup> A notable synthetic application of alkene hydrogenation in 2008 was disclosed by Burgess, who prepared a library of useful enantiopure acyclic 1,3-hydroxymethyl synthons.<sup>186</sup> Finally, two theoretical investigations have been published, by Ujaque<sup>187</sup> (comparing gold and palladium Schiff base complexes), and by Woo and Fogg<sup>188</sup> (mechanism of hydrogenation with ruthenium catalysts).

## 2.2 Imine and carbonyl reduction

Noyori has published a full paper on catalytic asymmetric reduction of ketones catalysed by Ru<sup>II</sup>(binap) complexes.<sup>189</sup> The work is specifically concerned with the relative contribution of hydrogenation and transfer hydrogenation pathways under various reaction conditions; excellent e.e. values are obtained throughout (97-98%).

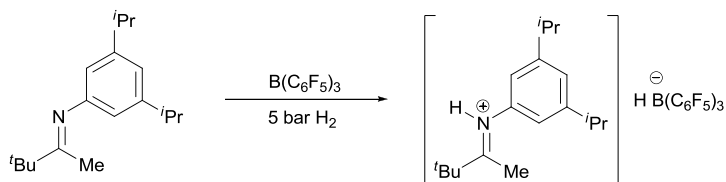
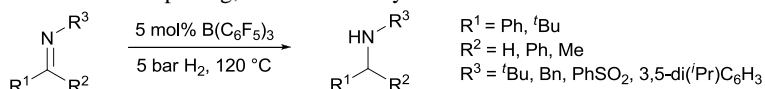
Another important advance in 2008 was reported by the You group, who have delineated the substrate scope for their asymmetric transfer hydrogenation of  $\beta,\gamma$ -alkynyl- $\alpha$ -imino esters catalysed by a homochiral Brønsted acid (Scheme 57).<sup>190</sup> A Hantzsch ester was employed as hydride donor, and a range of different ester- and alkynyl-substituted substrates were observed to undergo tandem alkyne-to-alkene and imine-to-amine reduction with good stereoselectivity (83-96% e.e.).



**Scheme 57**

A report from Stephan and co-workers describes imine hydrogenation catalysed

by a boron Lewis acid,  $B(C_6F_5)_3$ .<sup>191</sup> The methodology stems from the group's earlier report that hydrogen gas can be heterolytically cleaved by bulky boranes and phosphines, systems which they have termed "frustrated Lewis pairs" (Scheme 58). In the current work, they report that bulky boranes and imines also form "frustrated Lewis pairs" that effect hydrogen scission and imine reduction. A variety of aryl aldimines and ketimines are reduced in good yield; in one instance, excessive steric bulk on the imine prevented its reduction and the stable iminium borohydride was isolated instead. An example is also disclosed of the same catalytic system effecting reductive aziridine opening, and a related system is described for nitrile reduction.



**Scheme 58**

Other advances in imine reduction include the report by Guo and co-workers of 1-acetyl-2,3-dimethylimidazolidine as a novel organic reductant for transfer hydrogenation of aryl aldimines (also aryl and alkyl aldehydes) in good yield.<sup>192</sup> Chadha has reported a whole-cell bioreduction of *N*-aryl imines derived from aryl-substituted acetophenones.<sup>193</sup> The organism employed is *Candida parapsilosis* ATCC 7330 and the amine products are obtained in good yields and in excellent e.e. (95-99%); such enzymatic imine reductions are comparatively rare. Other enzymatic reductions reported in 2008 include asymmetric ketone reduction effected by immobilised *Geotrichum candidum* NBRC 5767,<sup>194</sup> asymmetric reduction of halo-substituted aryl ketones by *Rhizopus arrhizus*,<sup>195</sup> and Kroutil's highly ingenious application of concurrent, non-interfering enzymatic alcohol oxidations and ketone reductions to effect stereoinversion and deracemisation of secondary alcohols.<sup>196</sup> (A second report from Kroutil is specifically concerned with asymmetric reduction of bulky ketones<sup>197</sup>).

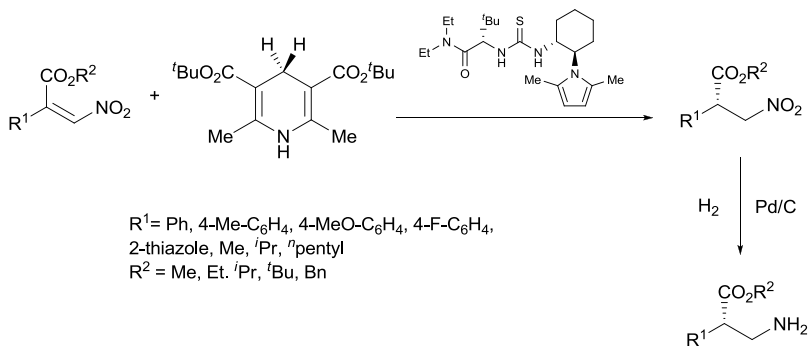
Also reported in 2008 are Krische's use of a rhodium complex to catalyse imine reduction with concomitant C-C bond formation<sup>198</sup> and an electroreductive approach described by Kise.<sup>199</sup> Peris has detailed an unusual example of base-free catalysed reduction of carbonyls and imines by transfer hydrogenation with an  $\text{Ir}(\text{Cp}^*)$  complex; the coupling of this transformation to an enzymatic dynamic kinetic resolution is also described.<sup>200</sup> Frejd has used chiral ligands containing bicyclo[2.2.2]octane motifs to effect asymmetric reduction of acetophenones with catecholborane.<sup>201</sup>

### 2.3 Conjugate reduction

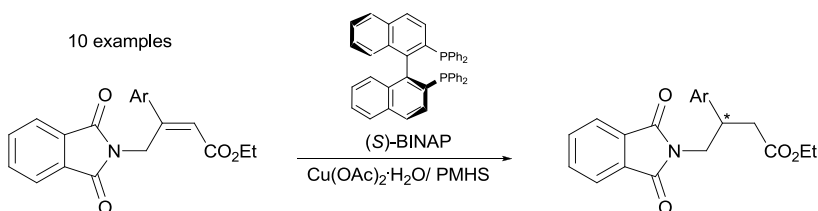
The List group have communicated methodology for accessing  $\beta^2$ -amino acids by means of an organocatalytic asymmetric conjugate reduction of  $\beta$ -nitroacrylates to the corresponding  $\beta$ -nitroesters and subsequent nitro group reduction.<sup>202</sup> The

reaction employs a thiourea catalyst and a Hantzsch ester as hydride donor (Scheme 59). Stereoselectivity is good, with e.e. values of 86-95% reported.

A conjugate reduction approach to amino acids was also reported by Hu and Zheng, although in this case the substrates targeted were  $\beta$ -aryl- $\gamma$ -amino acid derivatives and a copper catalyst was employed (Scheme 60).<sup>203</sup> E.e. values ranged from 91 to 96%, and the utility of the methodology was showcased with a concise synthesis of the pharmaceutical agent (*R*)-baclofen. Elsewhere, Sodeoka reported use of ethanol as solvent and reductant for Pd<sup>II</sup>(DUPHOS)-catalysed conjugate reduction.<sup>204</sup>

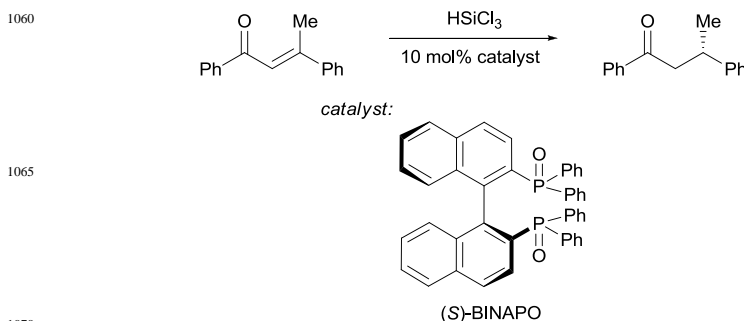


Scheme 59



Scheme 60

Sugiura and Nakajima have demonstrated that conjugate reductions of  $\alpha,\beta$ -unsaturated ketones with trichlorosilane may be catalysed with simple Lewis bases such as triphenylphosphine oxide or HMPA.<sup>205</sup> Excitingly, in preliminary investigations into the possibility of asymmetric induction in such transformations, the reduction shown in Scheme 61 could be effected in 97% yield and 97% e.e.



Scheme 61

The above catalytic system was also employed to effect reductive aldol reactions. Progress in reductive aldol methodology has also been reported in 2008 by the Lam group, who have reported conjugate reduction-aldol reactions catalysed by cobalt for the coupling of  $\alpha,\beta$ -unsaturated amides with ketones<sup>206</sup> and of 4-acryloylmorpholine with *N*-tosyl aldimines.<sup>207</sup> The group has also employed nickel catalysts for such conjugate reduction-initiated couplings, reporting a detailed study on diastereoselective nickel-catalysed reductive aldol cyclisations,<sup>208</sup> and subsequently applying this methodology in the synthesis of salinosporamide A.<sup>209</sup>

1080

## 2.4 Other reductions

In the field of magnetic nanoparticles, Frost and Price have reported new efficient rhodium catalysts supported on superparamagnetic iron oxide nanoparticles.<sup>210</sup> They proved to be highly active catalysts for hydrogenation of the test alkene substrates (1-hexene, 1-dodecene and dimethyl itaconate) and were easily recovered upon application of an external magnetic field.

In the field of alkyne reduction, the Elsevier group have addressed the problem of overreduction to alkanes by use of a palladium *N*-heterocyclic carbene complex.<sup>211</sup> Excellent chemoselectivity is claimed in the transfer semihydrogenation of numerous alkynes with this complex and formic acid as reductant; carbon dioxide is the only byproduct.

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1095

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